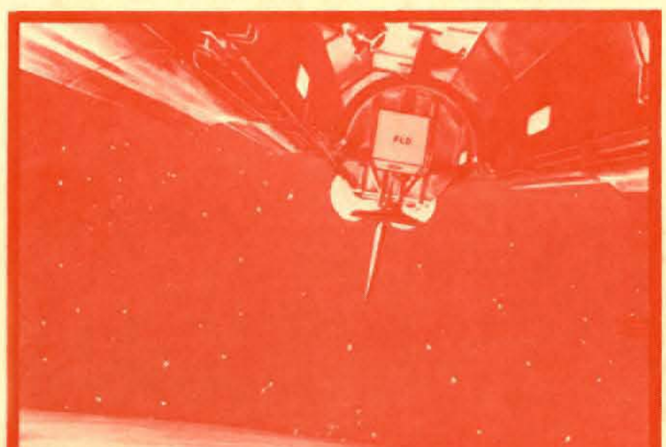
WORKSHOP ON

APPLICATIONS OF LUMINESCENCE TECHNIQUES TO EARTH RESOURCE STUDIES



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WORKSHOP ON

APPLICATIONS OF LUMINESCENCE TECHNIQUES TO EARTH RESOURCE STUDIES

Editors:
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A Lunar and Planetary Institute Workshop
December 10-12, 1980

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Contents

Introduction

Background

The Non-Renewable Resources Program within NASA's Office of Space and Terrestrial Applications periodically sponsors specialized workshops to discuss the future development of specific remote sensing techniques. The general purpose of these workshops is to: (i) summarize state-of-the-art capabilities of particular remote sensing methods, (ii) identify key technical issues related to future development, and (iii) discuss the logical progression of future R & D activities leading to improved capabilities. Workshops held in the recent past have focused on radar imaging methods (Radar Geology Workshop, Snowmass, Colorado, held in July, 1979) and thermal infrared techniques (Workshop on Geological Applications of Thermal Infrared Remote Sensing Techniques, Houston, Texas held in February, 1980). Attendance at these types of meetings is typically quite broad, involving individuals with backgrounds in scientific research, geological applications, and sensor engineering. At the same time, the number of participants is generally restricted to 30-50 individuals so that informal exchange of views and opinions is possible.

The impetus for a workshop on luminescence methods was provided by a proposal from the U. S. Geological Survey to conduct a luminescence imaging experiment onboard the Space Shuttle in the mid-1980's. NASA and the USGS had collaborated during the 1970's in the fabrication and field testing of a Fraunhofer line discriminator (FLD) instrument, an airborne device to measure the solar stimulated luminescence of natural surficial materials. Based upon the results of field experiments conducted with this instrument, USGS researchers proposed that a new scanner system be developed which could be used to obtain luminescence measurements at both aerial and orbital altitudes. In responding to this proposal, NASA suggested that a meeting be held to review the results of earlier field experiments, and to discuss the direction of future R & D.

The technical workshop described in this report was organized on the basis of this suggestion. The meeting was held at the Lunar and Planetary Institute December 10–12, 1980, and was co-sponsored by NASA and the U. S. Geological Survey.

Program Co-chairmen were Anthony Barringer (Barringer Research, Inc.) and William Hemphill (USGS). Approximately 35 individuals representing a variety of government agencies, private companies, and academic institutions attended the workshop (a list of participants is included in this document).

Purpose and Description

The purpose of the Workshop on Luminescence Techniques was threefold:

(1) to review the state-of-the-art capabilities of luminescence methods,
(2) to consider a variety of concepts for the development of future luminescence sensor systems, and
(3) to discuss appropriate research and development strategies for advancing the current state-of-the-art.

The review of past research results was directed towards identifying the various types of geological and environmental information that could potentially be obtained through the analysis of luminescence measurements. Previous laboratory studies of luminescence properties of natural materials and field results obtained with the FLD instrument were discussed in some detail. Workshop participants were asked to consider how geological information derived from luminescence measurements would complement information obtained by other remote sensing techniques.

The presentation of new concepts for future luminescence sensor systems covered a wide variety of options, ranging from airborne scanners to potential Shuttle and satellite instruments. These presentations emphasized the tradeoffs between sensitivity, and spatial and spectral resolution that would be required by currently available technology. Complications associated with the design of calibrated, multispectral sensor systems were considered, along with data transmission and processing requirements of particular instruments.

The latter portion of the meeting was devoted to future research activities which could contribute to improved understanding of the geological utility of luminescence methods. A wide variety of laboratory studies, ground-based field experiments, and theoretical modeling projects were discussed. Consideration of the various ways in which environmental stress can affect the luminescence properties of natural vegetation stimulated speculation regarding the potential utility of luminescence techniques for geobotanical mapping. In addition, general agreement was reached on the desirability of registering and analyzing luminescence measurements in combinations with other types of remote sensing data.

Outcome of the Workshop

Exchange of questions and opinions between the participants was open and frank, and the meeting was judged to be highly successful. A detailed summary of the findings and recommendations of the Workshop was prepared by Dr. Barringer and Dr. Thomas McCord (University of Hawaii). The workshop summary immediately follows this introductory section.

The discussions at the meeting highlighted the need for:

- Additional laboratory studies of the luminescence properties of naturally occurring surficial materials.

- Capability to measure the *in situ* luminescence properties of surficial materials under natural field conditions.

- Capability to accurately predict the amplitude of solar stimulated luminescence of surficial materials at orbital altitudes (i.e., above the earth's atmosphere).

- Capability to obtain simultaneous multispectral luminescence measurements at various spatial resolutions from an experimental airborne platform.

In the opinion of the workshop participants, applied research and instrumentation development required to address these needs should be conducted in a parallel fashion during the immediate future.

We believe that the results of the Workshop provide a firm rationale for the continued development of luminescence methods and a useful guide to the kinds of R & D activities that should be given priority attention in the future. On behalf of both NASA and the USGS we would like to thank all who participated in the workshop, especially the chairmen and summarizers, for their hard work and dedicated effort in making the meeting a success.

James V. Taranik
Program Chief

Mark Settle
Program Scientist

Non-Renewable Resources Program
Office of Space and Terrestrial Applications
NASA Headquarters

Summary

A. R. Barringer and T. B. McCord

This meeting was held to review the current status of luminescence remote sensing techniques, discuss their potential, and define future directions which might prove fruitful in developing and applying these methods. Much of the luminescence research performed to data has been conducted with the Fraunhofer line discriminator (FLD) instrument operated by the U. S. Geological Survey. This instrument measures the solar stimulated luminescence of the earth's surface within narrow wavelength bands where the intensity of natural solar radiation is highly attenuated by the sun's corona (i.e. the so-called "Fraunhofer lines" within the natural solar spectrum). Discussion of current capabilities focussed primarily upon results obtained with this instrument. A variety of individuals with personal experience in the analysis and interpretation of FLD data participated in the meeting. Future instrument design concepts that would provide improved measurement capabilities were also discussed. Spirited conversation occurred on the topic of what should be done next in developing luminescence methods. This section is an attempt at summarizing the results of the meeting.

Findings of the Workshop

There appears to be near unanimity of opinion on several basic points concerning the present situation:

1. The technique of FLD provides a method of looking at the earth which is entirely different from other remote sensors, and therefore generates a different kind of information.

2. The technique definitely has potential for a wide variety of remote sensing applications.

3. Sufficient work has been carried out over a more than ten year period by the USGS to show that this potential exists.

4. Further work in the laboratory and in the field is required to more fully define the value of FLD for its various geological, renewable resource, and environmental applications.

5. The existing airborne instrumentation needs to be advanced as soon as possible to the next stage to provide simultaneous data on more than one Fraunhofer line at considerably improved spatial resolution.

6. The integration of the FLD with other types of remote sensing data would greatly enhance its value and the development of interpretation techniques.

7. The FLD appears to have applications for spacecraft remote sensing and NASA is the appropriate agency to sponsor further development.

Work carried out by the USGS has already established in a preliminary fashion the feasibility of using an FLD scanner in some of the following application areas:

- Mapping of phosphate distributions as an aid to locating sources of fertilizer

- Hydrodynamic applications in tracing water flow movements in oceans, rivers, and lakes using dyes.

- Monitoring certain pollutants such as the effluents from pulp and paper manufacturing operations.

- Oil spill and seep detection and monitoring

- Mapping and discriminating geochemically and environmentally stressed vegetation
- Detecting luminescence associated with tungsten and uranium mineralization
- Mapping of ocean chlorophyll concentrations, plankton distribution, etc.

The accomplishments to data by the USGS on the FLD program working on a limited budget are praiseworthy and certainly provide the stimulus for an expanded effort.

Recommendations

Recommendations for future efforts also have a wide base of support among the meeting participants:

1. The potential of FLD merits further investigation at a higher level of funding.
2. Additional laboratory and field measurements are required with special reference to investigating the luminescence properties of natural surfaces and soils and their relationship to parent rocks and materials.
3. Additional laboratory and field measurements are required to supplement existing information on the effects of vegetation stress in relation to luminescence properties. This work should cover the fields of agriculture, mineral exploration, oil exploration, and environmental pollution.
4. The development of a hand-held field instrument is essential as an aid to accomplishing items 2 and 3 above.
5. Model and field studies are required to trace the relationship between surface luminescing materials and underlying mineralization and hydrocarbon accumulations.
6. An advanced airborne multiple-wavelength imaging FLD instrument must be built and flown over a variety of test sites. An adequate funding level is required in order to test and develop the method in a timely fashion, and a variety of other remote sensing measurements should be made in conjunction with FLD so that the potential of integrated application can be properly evaluated.
7. Steps 2, 3, 4, 5 and where and when possible 6, should be done interactively.
8. A shuttle experiment is required to determine the problems and potential of FLD for routine space applications.

Outlook for the Future

Because of limited funding and the use of aircraft of minimal size, the potential of FLD for use in an integrated mode with other remote sensing techniques has scarcely been explored. It seems almost certain, however, that solar and thermal infrared measurements could be very complementary to FLD — for example, in the measurement and intrepretation of plant stress. In the case of low-level surveys, the combined use of gamma ray spectromtery and FLD for uranium exploration looks promising, and the further addition of a magnetometer could be most valuable in some geologic and exploration applications. All remote sensing techniques are enhanced by their use in a complementary fashion, but it seems likely that this will be particularly the case with FLD.

PAPERS

COOPERATIVE ROLE OF NASA AND THE GEOLOGICAL SURVEY IN THE DEVELOPMENT OF TECHNIQUES TO MEASURE LUMINESCENCE,

William R. Hemphill, U.S. Geological Survey, Reston, Va. 22090

Although hand-carried ultraviolet lamps were used extensively in the 1940's and 1950's in prospecting for scheelite ($CaWO_4$), uranium, and other luminescing materials, the lamps were low powered and rarely effective more than a meter or two from the outcrop. The work had to be conducted at night in order to avoid obscuring the relatively weak luminescence by bright sunlight. In the mid-1960's the U.S. Geological Survey, in collaboration with the National Aeronautics and Space Administration (NASA), experimented with ultraviolet sources such as cathode ray tubes (1) and lasers. Although ranges of a few hundred meters were possible, the need for night operation restricted the usefulness of these ultraviolet sources.

The Fraunhofer line-depth method for measuring luminescence uses the Sun as an excitation source and permits detection of luminescing materials during daylight, thus avoiding the power and distance limitations of artificial sources and the awkward logistics of night time operations. This approach involves observing a selected Fraunhofer line in the solar spectrum and measuring the ratio of the central intensity of the line to a convenient point on the continuum a few angstroms distant; this ratio is compared with a conjugate spectrum reflected from a material that is suspected to luminesce. Both ratios normally are identical, but luminescence is indicated where the reflected ratio exceeds the solar ratio. The Fraunhofer method was first used by the astronomer Kozyrev (2) to detect luminescence in the ray systems of the lunar craters Aristarchus and Herodotus.

Work with a laboratory spectrometer showed that luminescence exhibited by mineral samples could be detected in daylight using the Fraunhofer line depth method. The Geological Survey proposed that an instrument employing the Fraunhofer method could be used from aircraft and spacecraft to detect luminescing materials on the Earth's surface (3).

The prototype airborne instrument employing the Fraunhofer line discriminator (FLD) was designed and constructed by the Perkin-Elmer Corporation[1/] under contract from NASA through their Supporting Research and Technology (SR&T) Program. Delivery to the Geological Survey occurred in the spring of 1968. Key components of the Perkin-Elmer design were two glass-spaced Fabry-Perot filters, which provided a single transmission spike abut 0.5 angstroms (Å) wide. The center wavelength was tuned by means of a temperature-controlled housing around the filter package. A 25°C change in temperature shifted the pass band about 1Å. One filter was tuned to the central intensity of the Fraunhofer line; the pass band of the other filter is on the continuum a few angstroms away.

Rhodamine WT dye is a water soluble luminescent dye used by hydrologists and oceanographers to study current dynamics in rivers and estuaries. Detection of rhodamine dye was a design goal in the FLD development, and sensitivity of the prototype was adequate to detect rhodamine dye in concentrations as low as 10 parts

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[1/] Use of trade names is for description purposes only and does not constitute endorsement of the product by the U.S. Geological Survey.

per billion (10 ppb). The emission peak of rhodamine dye is at 5800 Å; accordingly the sodium D Fraunhofer line at 5890 Å was used in the prototype. Outdoor tank, shipboard, and helicopter tests of the prototype instrument, as well as other potential applications of the FLD, are described by Hemphill and others (4).

Operation of the prototype FLD was limited to the 5890 Å Fraunhofer line. A laboratory fluorescence spectrometer was used to measure the luminescence intensity of materials at Fraunhofer lines other than the 5890 Å line. Rhodamine dye was used as a luminescence standard, and the emission of target materials at specific Fraunhofer lines was expressed in terms of rhodamine dye (5). Luminescence at as many as six Fraunhofer lines in the visible spectrum were cataloged for crude and refined oils, chlorophyll of various plants, municipal and industrial pollutants, and selected rock materials. These data helped to support the justification for an improved FLD. Funding support for an improved engineering model FLD was provided by NASA through their Advanced Applications Flight Experiments (AAFE) Program.

The engineering model FLD, also built by Perkin-Elmer Corporation, was delivered in 1974 and initially functioned in a radiometer mode from a helicopter. Sensitivity in terms of rhodamine dye was 0.1 ppb. The instrument could be operated at any one of the following three Fraunhofer lines: 4861 Å, 5890 Å, and 6563 Å. Results achieved in the helicopter tests are described by Watson and Hemphill (6).

In 1977, a scanner was added permitting operation in an imaging mode from fixed-wing aircraft. Although tests in this mode clearly demonstrate the improved capability to relate areal distribution of luminescence to specific features in the imaged scene, the spatial resolution of 45 m was impractically coarse in a swath width of 1600 m. Also, there was a recognized need to operate in at least two and preferably three Fraunhofer lines simultaneously, so that band ratioing and other data processing procedures could be performed. Figure 1 shows study areas where the FLD has been operated in both radiometer and imaging modes.

A new third generation instrument is feasible and could provide an instantaneous field of view of 3 m from an aircraft altitude of 2400 m, and simultaneous operation in two or more Fraunhofer lines. The primary function of the new instrument would be to continue the aircraft program already begun. However, it would be desirable to use the same instrument in an experiment aboard the space shuttle (single sortie of a few days) to determine the feasibility of performing luminescence measurements from space. A proposal for a shuttle experiment was submitted to NASA in October 1978.

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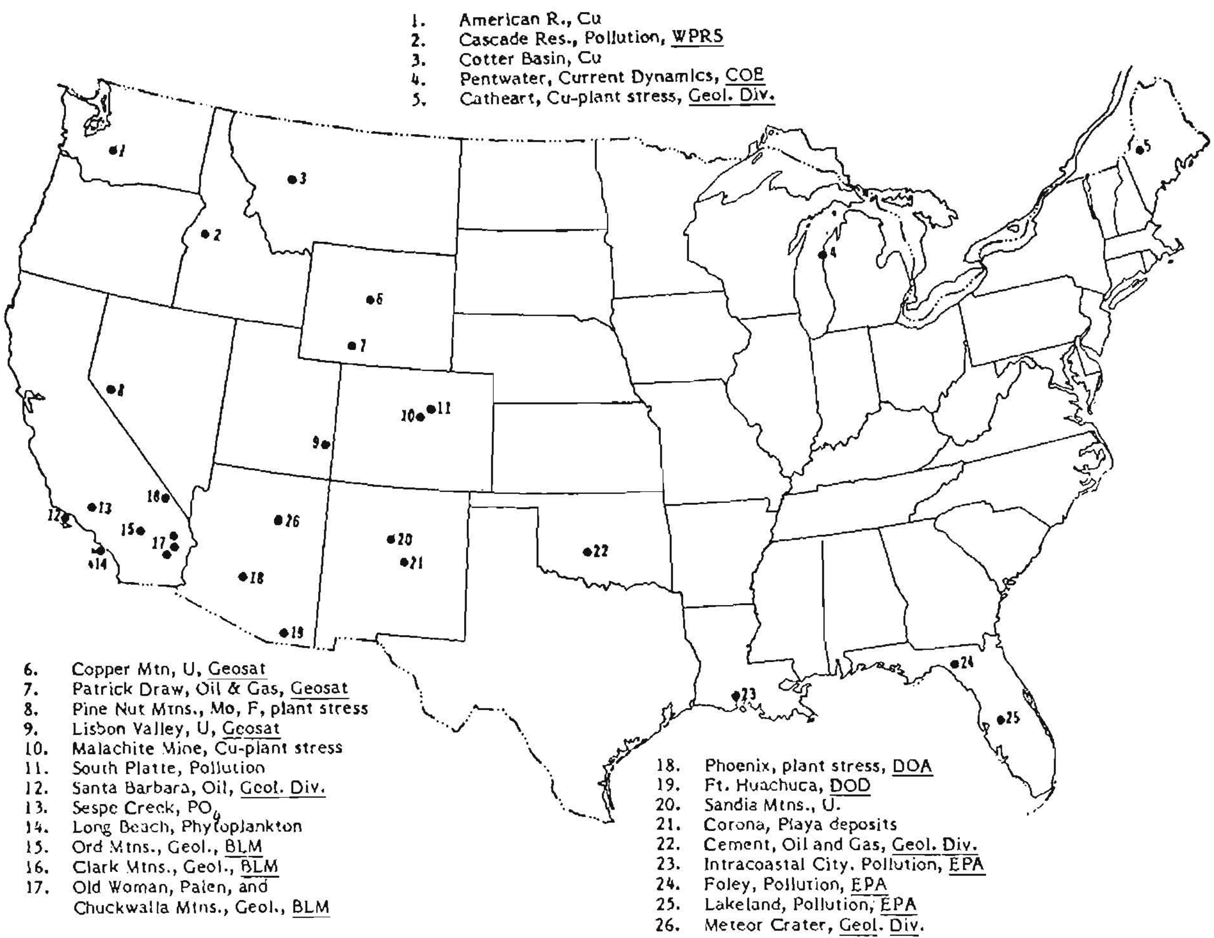

Figure 1.--Study areas where the FLD has been tested since 1974. FLD was operated in the radiometer mode in areas 4, 8, 10, 11, 13, and 22-25, and in the imaging mode in areas 1-3, 5-9, 12, 13, 15-21 and 26.

FUNCTIONAL DESIGN OF THE PERKIN-ELMER FRAUNHOFER LINE DISCRIMINATOR MK II, F. C. Gabriel and J. A. Plascyk, The Perkin-Elmer Corporation, Norwalk, CT 06856

The Fraunhofer Line Discriminator MKII* (FLD-II) is an airborne computing photometer that determines and displays real-time values of the luminescence and reflectance of a scene within its field of view.[1,2] Using the sun to excite this luminescence, the photometer then must distinguish the solar illumination from the luminescence that may be orders of magnitude weaker. FLD-II measures luminescence in a scene by quantitative distinction between reflected sunlight, which is "coded" by narrow Fraunhofer absorption lines, and luminescence, which is not.

The Fraunhofer lines of interest are generally very narrow (less than 0.1 nm) and are appreciably reduced in intensity from the continuum. Narrow-band (0.07 nm), high efficiency optical filters in the FLD-II are used to provide in-band and out-of-band light samples from the scene and pure sunlight to a photomultiplier tube. The FlD-II used solid-etalon Fabry-Perot filters that are fabricated by Perkin-Elmer under a patented technique**. This thin, solid-spaced, fused-silica etalon, supported on a thick fused-silica substrate, is rugged and stable.

To permit operation over widely varying light conditions, including cloud cover, the instrument uses a high-gain photomultiplier tube that has automatic gain control. This tube detects the energies received from the FLD-II's earth-looking telescope and sky-looking telescope (via a diffuse sun target). These energies are sampled alternately through a rotating chopper. Each of the signals received from the telescopes is further split by the chopper to provide both a signal representing the Fraunhofer line and a signal that represents the continuum spectrum on either side of the line. Thus, the detector sees four separate signals in sequence. Figure 1 illustrates the principles of the FLD-II technique. These measurements are repeated at the rate of 40 Hz.

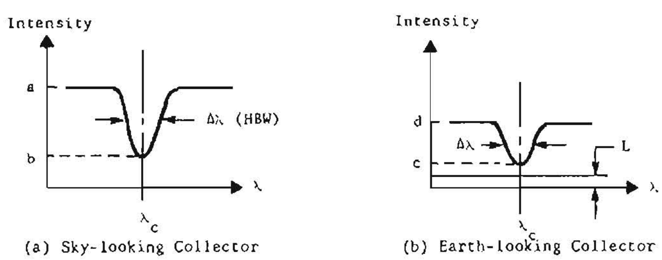

Figure 1. FLD-II Technique Principle

*Designed and fabricated under Contract 14-08-001-13520 for the U.S. Geological Survey, U.S. Patent No. 3,769,516 issued to the Perkin-Elmer Corporation.

**U.S. Patent No. 3,578,848 issued to the Perkin-Elmer Corporation.

Gabriel, F. C. and Plascyk, J. A.

The signals are then integrated, digitized, and stored for use by a computer in the FLD-II console. The integration time is indicated by the setting on the console bandwidth-select switch, which can be varied in steps from 0.078 Hz to 20 Hz. The computer is a hard-wired digital unit and executes the calculation for luminescence, L, which is

$$L = \frac{d}{a} - \frac{d - c}{a - b} = \frac{d}{a} - R$$

where

a = Sky-continuum signal
b = Sky-Fraunhofer line signal
c = Earth-Fraunhofer line signal
d = Earth-continuum signal
R = Reflectivity

Both L and R are converted from binary to decimal numbers and are read out as displays on the front panel of the FLD-II console. These signals are also available in analog form, as are the individual signals a, b, c and d. These individual signals can be obtained from BNC connectors on the front panel.

The FLD-II was designed to have a 1° field of view, an etalon diameter of 25 mm, and a collector diameter of 50 mm. It was engineered to view the nadir from either a helicopter or fixed-wing aircraft. The instrument consists of a sensor head, which was designed to mount on the exterior of an aircraft, with an accompanying console mounted on a standard ATR rack inside the aircraft.

Figure 2 gives a view of the sensor. Weighing 80 lbs., the sensor's size dimensions are 18 x 18 x 12 in. The console weighs 50 lbs. with respective dimensions of 12 x 10 x 15 in. At 110 VAC, 400 W is the required power. FLD-II currently operates at any one of three Fraunhofer lines: 486.1 nm (H-β line), 589.0 nm (Na-D_2 line) and 656.3 nm (H-α line). Filters at other wavelengths can be provided.

Figure 2. Fraunhofer Line Discriminator Mark II, Equipment Packages

FLD-II has detected concentrations of the dye rhodamine WT in water down to levels of 0.1 ppb (1 part in 10^{10}) at the 589.0 nm Fraunhofer line in tests prior to delivery to the U.S. Geological Survey. Figure 3 illustrates the test results. FLD-II is a proven instrument documented by the U.S. Geological Survey in many field measurements during the last six years.[3]

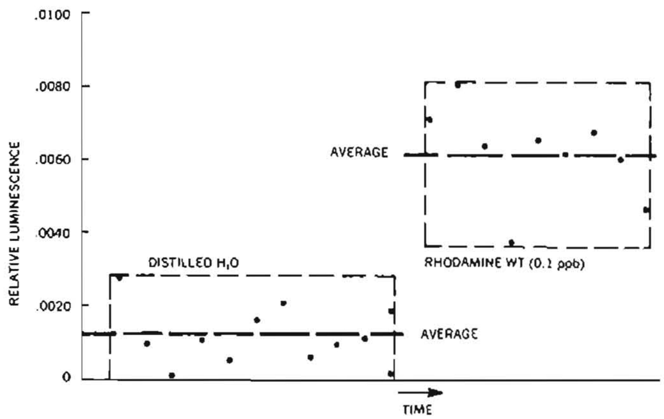

Figure 3. FLD MK II - Sensitivity Test

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3. Many of the papers contained within this volume.

ELECTRONIC AND OPTICAL MODIFICATION OF THE ENGINEERING MODEL FLD AND THE EVOLUTION OF PERIPHERAL EQUIPMENT,
Robert D. Watson, and Arnold F. Theisen, U.S. Geological Survey, Flagstaff, Az.

The engineering model Fraunhofer line discriminator (FLD), built by the Perkin Elmer Corporation[1/] and delivered to the U.S. Geological Survey in 1974, was designed to be used as an airborne radiometer operating from a helicopter. The FLD performed satisfactorily but only when operating with an instrument bandwidth of 0.1 hertz (Hz). Bandwidth limiting was required because the helicopter rotor caused interference with light viewed by the sky telescope. Whenever the sky telescope was shaded by the rotor, the automatic gain control, which was keyed to the sky continuum signal, increased the detector gain; the result was spiking in the output signal (fig. 1). Ground-based measurements not involving the helicopter rotor had demonstrated that luminescence variations were not significant (less than 1 percent) when viewing solid surfaces in a fixed position in the field of view, even at bandwidths > 0.1 Hz.

In 1977, FLD measurements from a fixed wing aircraft, using the FLD maximum bandwidth of 40 Hz, demonstrated that excellent results could be obtained over both water and ground targets. The only major difficulty encountered was the requirement of mounting the sky telescope through the top of the aircraft. This problem of structurally modifying the aircraft led to the investigation of Fraunhofer line depth as a function of both sky conditions and time of day. As long as the Sun was above 30° on either cloudy or sunlit days, the Fraunhofer line depth ratio (line center to continuum) changed by less than 1 percent which is within the experimental error of the FLD. Based on these measurements, the sky telescope was replaced with a standard lamp which has a variable aperture for adjusting the light intensity for the 486.1-, 589.0-, and 656.3-nanometer wavelengths.

In addition to operating the FLD as a radiometer, a system was designed in 1977 to permit the FLD to operate in an imaging mode. The FLD imaging system (fig. 2) is based on a simple optical-mechanical arrangement which uses a pair of front surface mirrors, one fixed at 45° with respect to the FLD earth telescope and the other oscillated about an axis which is parallel to the fixed mirror. The amount of oscillation provides a total sweep of $\pm 18.5^{\circ}$ with respect to the axis of the optical system or a total scan angle of 37°. The linearity and total angle of oscillation is controlled by a precision cam, based on an Archimedes spiral design. The rate of oscillation is determined by an electronically controlled precision DC motor with tachometer feedback. The feedback signal is monitored for accurate speed control of one complete sweep (37°) per second. A timing disk is mounted on the motor shaft to provide a beginning of sweep trigger, generated by an electro-optical coupler. Ground resolution is determined by the instantaneous 1° field of view of the FLD. Maximum ground coverage (without overlap) is obtained when the aircraft speed matches the ground resolution of the FLD. For example, with the present system, an aircraft speed of 45 meters/second (148 feet/second) and an altitude above terrain of 2,382 meters (7,815 feet), complete coverage would be provided by a square 45 meters (148 feet) on a side. However, because the instantaneous field of view is a circle 45 meters (148 feet) in diameter, the actual ground coverage is only 80 percent. A bore sight television system is used to identify surface features and to correlate these features with measured luminescence and reflectance.

1/ The use of trade names in this publication is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

Modification of the FLD

Watson

Data were originally acquired from the FLD by reading the luminescence or reflectance values displayed on the front panel of the electronics console unit (ECU). These values, or binary coded decimals (BCD's), were updated at a rate of two per second. They were recorded by voice on the audio track of a video tape used for recording the ground trace of the helicopter flight path.

A Hewlett-Packard digital printer was added to record the two-per-second BCD output provided by the FLD. Although this printer eliminated the need for a person to record in-flight data, it complicated the correlation of the data with the flight path.

A significant improvement was made with the addition of a second video camera focused on a light emitting diode (LED) display in a light-tight box. The LED presents the same values of reflectance and luminescence as the ECU display, at the same rate. The values are superimposed on the video image of the ground trace scene which permits correlation with the flight path. A clock has been added to show the month, day, hour, minute, and second.

The inherent maximum rate that data can be updated by the FLD is 40 per second. By modifying the display circuitry, this maximum rate is now available for the displays on the front panel of th ECU and the light-tight box via the BCD output. The digital printer cannot handle the higher rates of data now available and has been eliminated. The maximum rate of data that can be retrieved on playback of the video tape is 20 per second, because of phosphor decay of the video screen.

Another significant improvement in FLD operation was made with the addition of a Motorola-M6800 micro-processor. The system uses a 1-megahertz (Mhz) clock and has an interface board specifically designed for use with the FLD. The M6800 is programmed to organize FLD data in sweeps of 36 resolution elements. The FLD provides data at 40 Hz plus a data valid pulse. The beginning of the sweep trigger, the data valid pulse, and FLD imaging system data are fed into the computer where the beginning of sweep trigger produces a beginning of sweep mark, updates the sweep counter, and sets the computer to accept FLD data valid pulses and data. Sweep counts and beginning of sweep mark are transfered to a video monitor and recorder. Sweep counts and sweep mark are also recorded on a digital cassette tape. The data valid pulse causes the computer to transfer to digital tape both the luminescence and reflectance values for each resolution element up to 36 resolution elements per sweep. The 18th luminescence reading is also sent to the video display. The remainder of the time, in which four resolution elements would have been acquired, is used for return of the scan mirror to the start position.

FLD data, recorded on digital tape, are transferred to computer memory, where either luminescence or reflectance data for each resolution element can be analyzed and assigned a character representing either a specific value or a range in values. These characters are then reproduced by a printer with a capability of producing 94 distinct characters plus a blank. The computer is programmed to produce gray scale slicing with a preselected window for luminescence or reflectance.

When a part of the data has been selected for further processing, a histogram is printed utilizing the M6800. The data are transfered to a Digital Equipment Corporation PDP 11/45 mainframe computer and compressed to eight-bit format similar to that of Landsat data. The full range of processing, correction, and enhancement programs used on Landsat data can be applied to the FLD data, and the finished product can be presented in color form.

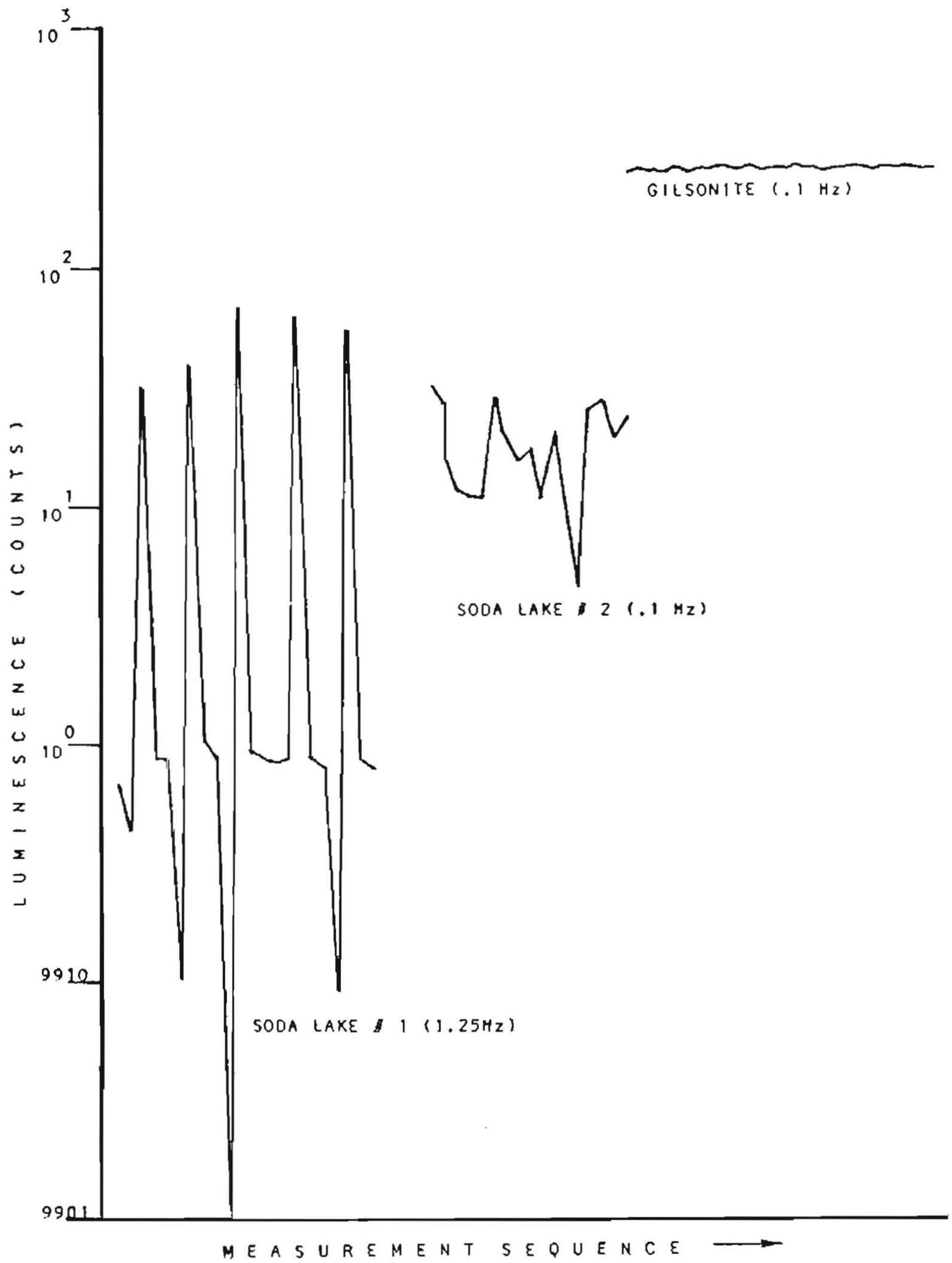

Figure 1. Luminescence measurements showing the effects of the helicopter rotor and bandwidth. The measurements at the Soda Lakes near Morrison, Colorado were made from a helicopter; the measurement of gilsonite was made in a ground test set-up. Spikes in the signal at Soda Lake #1 are caused by helicopter rotor interference, and are greatly reduced by bandwidth limiting to 0.1 Hz at Soda Lakes #2. The spikes are absent in the ground based measurement of gilsonite.

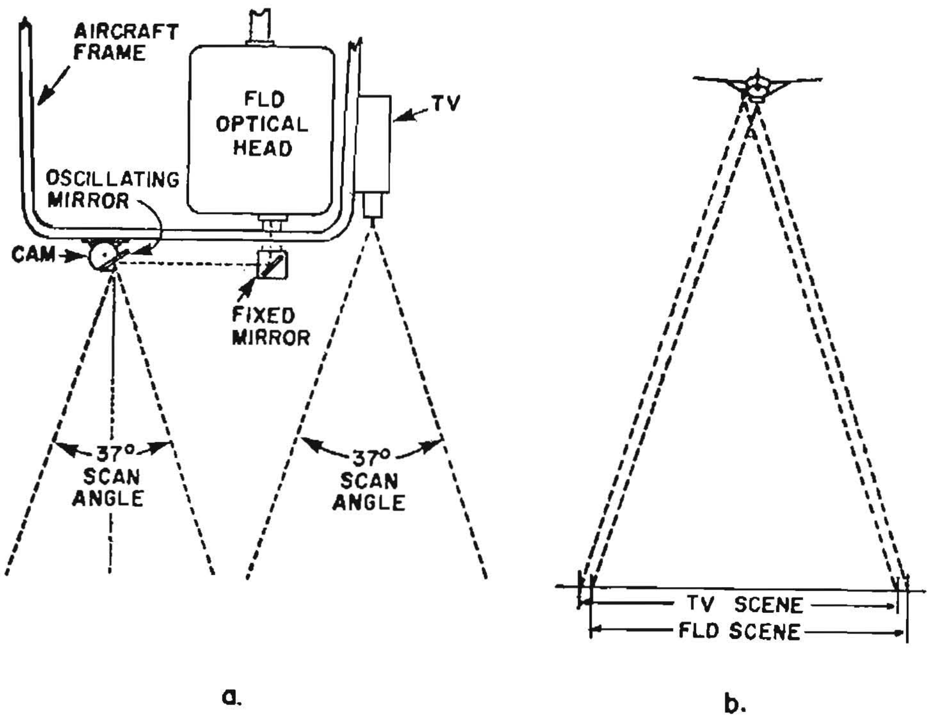

Figure 2. FLD imaging system. a. Diagram of the FLD imager showing components; b. schematic overview of ground coverage by the FLD and television system.

QUANTIFICATION OF LUMINESCENCE INTENSITY IN TERMS OF A RHODAMINE WT STANDARD, Robert D. Watson, U.S. Geological Survey, Flagstaff, Ariz.

Rhodamine WT is an artificial, water-soluble, organic dye used as a tracer by hydrologists and oceanographers to monitor the dynamics of currents in rivers and estuaries. In 1969 rhodamine dye was detected in seawater in concentrations of less than 5 parts per billion (ppb) with the aid of a prototype Fraunhofer line discriminator (FLD), an optical-mechanical remote sensing device, which has been used in the detection of solar-stimulated luminescence from aircraft. Experiments with a laboratory fluorescence spectrometer indicate that luminescence of many materials including rocks and minerals, crude and refined petroleum, stressed vegetation, open-ocean chlorophyll, and various man-made and natural pollutants, fall in range of the luminescence intensity of rhodamine dye in concentrations ranging from 0.1 ppb to 100 ppb. A Perkin-Elmer MPF-3[1/] fluorescence spectrometer with a correction microprocessor was used to quantify luminescence of materials of interest using rhodamine WT as a standard. Corrections were programed to automatically adjust for the wavelength dependence of the source and detector and to produce a correct distribution of relative luminescence intensity with wavelength.

The MPF-3 includes both excitation and emission monochromators, which permit the analysis of a sample in terms of either its emission spectrum or excitation spectrum. An emission spectrum is measured by keeping the wavelength of excitation constant and plotting the intensity of luminescence as a function of wavelength. An excitation spectrum is measured by keeping the wavelength of emission constant and plotting the intensity of luminescence as a function of excitation wavelength. Excitation spectra are analogous to the configuration of an FLD wherein the luminescence measured is observed within the narrow wavelength of a Fraunhofer line, and the excitation is from broadband solar illumination. Excitation spectra were used to quantify the luminescence of materials in terms of a rhodamine dye standard.

The geometry of measurement with the MPF-3 is shown in figure 1. Solid samples, or liquid samples in a centimeter quartz cell, are positioned in the sample compartment so that both excitation and emission are through the front surface of the sample. The sample surface is illuminated at an angle of approximately 30° to the normal, and luminescence emission is directed in a narrow solid angle (centered at 90° from the incident beam) from the sample surface to the detector.

In order to relate all luminescence spectra to one set of conditions, rhodamine WT is used as the reference or "standard" prior to each measurement. The relationship between dye concentration and luminescence intensity L,[2/] is expressed through Beer's law as :

$$L = I_o (1-\exp[-Kd])\,\phi$$

where L = total luminescence intensity, quanta per second (emitted in all directions); and

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1/ The use of trade names in this publication is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

2/ The luminescence intensity, L, as defined in these studies is the emission arising from excitation throughout the visible spectrum from the ultraviolet to the emission wavelength. The area under the excitation spectrum can be used when expressing L.

I_o = intensity of exciting light, quanta per second;

K = extinction coefficient;

d = optical depth; and

ϕ = quantum efficiency (yield) of luminescence.

When the solutions used are so dilute that self-absorbed light is small, this equation reduces to:

$L = (I_o \xi cd) \Phi$, where

$K = \xi c$;

ξ = molar extinction coefficient; and

c = molar concentration.

If the luminescence intensities of two solutions are measured with the same apparatus --with the same exciting source, detector, and geometry--the intensities are related as:

$$L_2/L_1 = \Phi_2/\Phi_1 \cdot d_2/d_1 \cdot c_2/c_1 \cdot \xi_2/\xi_1.$$

Therefore, the concentration of solution 2 is related to that of solution 1 as :

$$c_2 = c_1 \cdot L_2/L_1 \cdot \Phi_1/\Phi_2 \cdot d_1/d_2 \cdot \xi_1/\xi_2.$$

A precise quantification of the concentration of c requires not only a knowledge of the luminescence ratio, but also the ratio of both quantum efficiency, optical depth, and molar extinction.

A semiquantitative approach has been taken in these studies, which permits the luminescence of a sample to be expressed in terms of an equivalent concentration of rhodamine WT dye. When the area under the curve of the excitation spectra of a sample is compared to the area under the curve for rhodamine WT dye (at a specific dye concentration), a relative equivalent rhodamine WT concentration is obtained. For example, when a sample having an integrated excitation intensity of 50 is compared to a rhodamine WT concentration of 10 ppb, which also has an integrated excitation intensity of 50, the sample is said to have an equivalent luminescence of 10 ppb rhodamine WT. The merit in this approach is that it allows for correction of instrument response variations during measurement. Also, results achieved in the laboratory can be assessed in terms of whether or not the same material in the field would be within the sensitivity range of an airborne FLD. The term "relative" has been used, since quantum efficiency need not be determined for making the comparison just described.

To obtain the same wavelength and intensity dependence of luminescence in the laboratory as would be observed with an FLD, the source-detector corrected spectra must be convoluted with the spectral intensity of total solar radiation (direct plus diffuse). Although direct sunlight and diffuse skylight vary diurnally and seasonally, the solar-corrected spectra are referenced to a standard set of conditions: irradiation normal to the Sun's rays at sea level, airmass=2, solar constant=1.9 cal cm^{-2} min^{-1}, diffuse radiation for a typical midday, and midsummer clear weather as measured by Luckiesh (1). A depth correction is necessary since the FLD sensitivity was established by measuring rhodamine WT in a 1/2-meter deep tank, while laboratory samples are measured in a 1 centimeter cuvette. FLD measurements, therefore, are theoretically 50-times more intense than laboratory measurements on the same concentration of dye. When using distilled water as a rhodamine WT solvent, attenuation in the 1/2-meter pathlength reduces the FLD measurement to 48-times that of the laboratory measurement. In order to normalize FLD measurements to laboratory measurements, the FLD results are divided by a factor of 48. Greater accuracy can be achieved by measuring the optical depth of the material of interest and including this factor in the depth correction (2).

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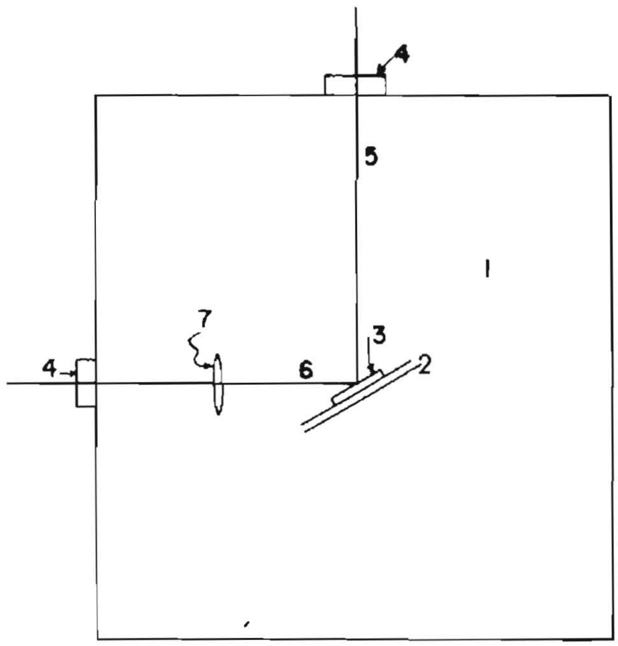

Figure 1. Sample area for measurement of luminescence: 1, sample area of MPF-3; 2, sample holder; 3, sample; 4, slit; 5, monochromatic exciting light; 6, luminescence emitted; and 7, collimating lens.

EXPERIMENTAL USE OF LUMINESCENCE TO IDENTIFY MOISTURE STRESSED VEGETATION AND POTENTIAL SIGNIFICANCE TO GEOCHEMICALLY INDUCED PLANT STRESS, Ray D. Jackson, U. S. Water Conservation Laboratory, Phoenix, AZ 85040

Methods of quantifying plant water stress using remotely sensed radiation emitted in the thermal infrared portion of the electromagnetic spectrum have been reasonably well developed (2,4). Remote sensing techniques using broad bands in the visible and shortwave infrared are sensitive to water stress primarily because of changes in plant canopy architecture and amount of green biomass. Chlorophyll fluorescence tends to increase as the photosynthetic apparatus of the plant begins to shut down in response to water stress. Thus, measurement of luminescence in certain Fraunhofer lines can also be used to detect plant water stress (6). Because of the demonstrated usefulness of a Fraunhofer Line Discriminator (FLD) for detecting geochemical stress in trees (1), and its potential usefulness in detecting water stress in citrus (6), additional experiments were conducted to determine if the FLD could detect plant water stress in field crops. Measurements were made in an alfalfa field where differential irrigation treatments produced plants with several degrees of water stress. This report first reviews the citrus experiment (6), and then describes results from the alfalfa experiment.

Irrigation water was withheld (except for a 12 mm rain) from thirteen mature lemon trees for three weeks prior to the measurements. At the initiation of the experiment, alternate groups of trees were irrigated to create a condition of non-stress in some, while retaining some trees under stressful conditions. The FLD measured the chlorophyll fluorescence of the trees from a platform about 12 m above the ground. Water potential measurements using the pressure bomb technique (8) were made on twigs clipped at chest height from four points around each tree. Diffusive resistance of the stomates on single leaves was determined by measuring the rate of water vapor evolution in a porometer. Samples for diffusive resistance were taken at chest height from eight points around the perimeter of each tree.

Twig water potential measurements indicated that all trees were under similar stress prior to irrigation. Afterwards, the irrigated trees were clearly less stressed than the non-irrigated trees. Although the stomatal diffusion measurements showed a separation of non-stressed and stressed trees in the afternoon samplings, there was no significant difference in the morning or at noon. Similarly, the data from the FLD showed no differences in fluorescence between the irrigated and non-irrigated trees in the pre-noon measurements, but differences were evident in the afternoons. The most significant separation of values occurred at 1500 hrs.

The difference in fluorescence patterns between irrigated and non-irrigated citrus demonstrated the utility of the FLD for the previsual identification of water stress in trees and suggested that it may be useful for other crops. These results also support the earlier work on detection of geochemical stress.

The alfalfa experiment was conducted on four differently irrigated plots in a 2-ha field. The FLD was mounted on a boom protruding from a truck. Measurements were made over test areas several meters long within the plots.

Broad band reflected and thermal radiation were measured over the same areas, using hand-held radiometers (5). Plant water potential measurements were made using the pressure bomb technique (8) on plant stems sampled near the measurement areas. Measurements were made at several times during the day. However, high air temperatures experienced in the afternoon caused a malfunction of the FLD, leaving only data from a morning run (1000 hrs.) available for analysis.

Plots of raw luminescence values versus plant water potential, which was normalized to account for vapor pressure differences (3), showed no relationship (the cross symbols in Figure 1). The most highly stressed plot (according to both plant water potential and thermal IR measurements) had a raw luminescence value only slightly less than the well-watered plot. This was contrary to theoretical expectations of increasing luminescence with increasing stress. One explanation for this apparent anomaly is that the stressed plot had less biomass and hence less chlorophyll available to fluoresce, a problem not encountered with the citrus trees. Since a vegetation index, calculated as the ratio of the broad band shortwave IR to the visible red radiance, is proportional to the green biomass viewed by a radiometer (9), this ratio was used to normalize the raw luminescence values. Figure 1 shows a plot of the normalized luminescence versus the normalized plant water potential. The circular symbols, and the lines connecting them, indicate that the luminescence increased with increasing stress.

The tree experiment demonstrated that FLD measurements are capable of detecting stress in situations where the plant biomass does not markedly change. However, in alfalfa, canopy architecture, wilting, and biomass changes complicate the interpretation of FLD data because varying amounts of soil are visible to the sensor. These effects must be taken into account before stress can be identified. In conjunction with other measurements, such as the IR/Red ratio, the FLD may be useful in detection of water stress, but would probably not be as simple to use as the thermal IR technique. On the other hand, the thermal IR can detect stress but cannot readily determine its cause. Water, disease, and nutrient stress all appear similar from a thermal standpoint. These experiments, and those of Rao et al. (7), suggest that the FLD may prove useful in differentiating the cause of stress, when used in conjunction with other sensors. Although these results are not conclusive, they show the need for a state-of-the-art instrument (one that will withstand high ambient temperatures). More experiments under well controlled conditions are required to further substantiate these results.

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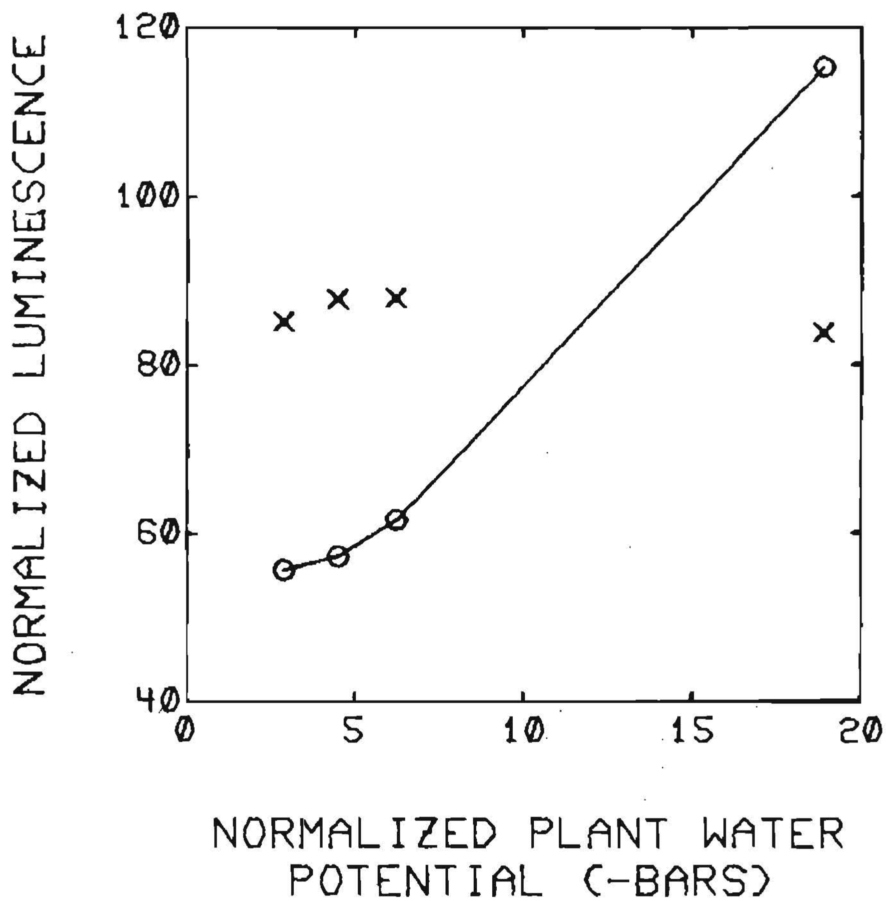

Figure 1. Normalized luminescence versus normalized plant water potential (circular symbols). The crosses represent raw luminescence values that were divided by 10.

ENVIRONMENTAL POLLUTANTS DETECTION WITH THE FLD, J. McFarlane, U. S. Environmental Protection Agency, Terrestrial Division, Corvallis, Oregon 97330.

The Environmental Protection Agency has been charged with implementing many provisions of the public law. For instance, EPA has the major responsibility for the Resource Conservation and Recovery Act, the Federal Insecticide, Fungicide and Rodenticide Act, the Federal Water Pollution Control Act, the Clean Air Act, and the Toxic Substance Control Act. To some extent, each law requires monitoring of pollutants in various media. We are also charged with determining exposure assessment and making damage estimations, from anthropogenic pollutants. Measuring where pollutants are and how they are moving or may potentially move in various environmental media is a prime concern to the Environmental Protection Agency. Our interest in the capacity of the Fraunhofer Line Discriminator is, therefore, based on its potential to do two jobs: 1) to remotely detect various pollutants, and 2) to observe the environmental impact of pollutants. Both purposes seem obvious, the latter, however, is far more difficult to achieve. Many environmental pollutants fluoresce in natural sunlight. The ability of the FLD to detect this fluorescence without the required addition of stimulating radiation offers a significant advantage. Some pollutants suppress the vigor and growth of plants by interferring with the photosynthetic process. When this occurs, often the excess energy is removed by fluorescence. Thus, measurement of plant fluorescence offers a potential of identifying areas of pollutant stress which were previously impractable with conventional stress measurements.

I will report on three separate experiments which demonstrate the utility of the FLD in the measurement of environmental contaminants.

<u>Lignin Sulfonate (1)</u>

In the process of making paper from pulp, spent sulfite liquor is often discharged. The liquors are injurious to fish due to their high oxygen demand. Lignin sulfonate is a constituent of the liquor that exhibits inherent lumenescence. In order to demonstrate the usability of the FLD in identifying spent liquors, samples were collected at the Buckeye Cellulose Plant in Foley, Florida, and their fluorescence spectra was determined. Next the FLD was operated at 486.1 nm from a helicopter hovering 30 m over the sampling points. High fluorescent levels were measured in the clarifying pond and the oxydizing lagoons. The upstream river showed little luminescence, but slightly elevated values were observed downstream. This increased luminescence indicated a small discharge of fluorescent material into the river. Thus, although the treatment facility appeared to be quite effective and no major contamination was observed, the FLD demonstrated the usefulness of this type of monitoring.

McFarlane, J.

Phosphate Processing Plant Effluents (1)

Phosphate rock generally contains quantities of uranium and its decay products radium-226 and radon-222. In the process of preparing phosphate rock to produce phosphoric acid and fertilizers, the possibility of environmental contamination with these radioactive products exists. An experiment was conducted near Lakeland, Florida, in which phosphorus luminescence was measured with the FLD. Measurement of different treatment and holding facilities in the phosphate plant clearly indicated high levels of fluorescence. Seepage of phosphate effluent into streams and ponds was also easily identified.

Oil Spill (2)

On October 16, 1975, while drilling for oil near Intercoastal City on Vermillion Bay, the well casing ruptured under high pressure and a 300 ft. geyser of oil was produced that distributed oil over many square miles of marshland and some agricultural areas. The geyser continued to fountain for several weeks spreading its film of oil in all directions depending on the speed and direction of the wind. The extent of oil distribution and the potential impact of this contaminating episode offered an interesting opportunity to determine the feasibility of mapping such a contamination with the FLD. A series of parallel flight lines were used and the FLD mounted in a helicopter collected data along these flight lines. Increased fluorescence was shown to correlate closely with the concentration of oil found on plant material as determined by extraction and analysis. Pollutant mapping, using conventional techniques of sample collection, elution, and analysis would require large numbers of samples and great analytical expense and generally would be considered impractical. However, the FLD demonstrated its capacity to map not only the presence but relative concentration of this environmental pollutant over a large area in a relatively short time.

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AIRBORNE FRAUNHOFER LINE DISCRIMINATOR SURVEYS IN SOUTHERN CALIFORNIA, NEVADA AND CENTRAL NEW MEXICO,

Robert D. Watson, U.S. Geological Survey, Flagstaff, Az.

The ability to detect luminescence rocks and minerals has been restricted in the past to night time operations because artificial excitation sources are relatively low-powered and for daytime operation, the presence of the bright solar background masks the weaker luminescence signals. The Fraunhofer line discriminator (FLD) overcomes these problems and permits the detection of solar stimulated luminescence several orders of magnitude less than the intensity detectable with the human eye. The FLD has been used experimentally to image the luminescence of phosphate rock and gypsum, fluorite, and playa deposits in selected sites in California, Nevada, and New Mexico.

The luminescence of 10 phosphate rock samples from the United States, Colombia, and Brazil were measured with a laboratory fluorescence spectrometer at the 486.1 nanometer (nm) Fraunhofer line to assess potential use of the FLD in prospecting for phosphate rock. These measurements, reported by Hemphill and others (1) and by Watson and Hemphill (2), showed luminescence intensities up to 8.0 parts per billion (ppb) rhodamine WT equivalency. All samples luminesced within the sensitivity range of the FLD, suggesting that it might be useful to experiment with this instrument in an airborne mode for field studies of phosphate luminescence.

The southeast-trending belt of the Santa Margarita Formation (late Miocene) in southern California (3) includes phosphate rocks in the Sespe Creek area of western Ventura County, about 40 km northeast of Santa Barbara. Laboratory spectral measurements confirmed that samples of phosphate rock and associated gypsum from the Santa Margarita Formation in this area luminesce within the sensitivity range of the FLD.

In field experiments in November 1974 and May 1975, the FLD was mounted in a helicopter and operated in the nonimaging radiometer mode. Luminescence was measured on helicopter traverses (fig. 1) and hovers above the Santa Margarita Formation as well as over detrital material downslope from that formation. This work showed that although luminescence of both the phosphate rock and gypsum are similar, the two materials can be distinguished because reflectance of the gypsum exceeds that of phosphate rock by as much as a factor of five. Details of the 1974-1975 helicopter work are described by Hemphill and others (1) and by Watson and Hemphill (2).

On November 6, 1979, the FLD imaging system, operating at 486.1 nm, was used to acquire an image (fig. 2) from a fixed-wing aircraft of the same area previously overflown with the helicopter. Luminescence values are color coded in the image with dark blue as the lowest value through red as the highest. Also shown in figure 2 is a geologic map of the Sespe Creek area (4). High luminescence values, shown in red (>3.9 ppb rhodamine dye equivalency), correlate well with the phosphatic Santa Margarita Formation. Values exceeding 2.2 ppb rhodamine dye equivalency (yellow, orange, and red) south of the Santa Margarita Formation are believd to be from detrital material (phosphate rock and gypsum) washed down slope from that formation. Luminescence values greater than 2.2 ppb rhodamine dye equivalency are rare south of Sespe Creek where the Santa Margarita Formation is absent.

Watson

The Pine Nut Mountain area, 17 km southeast of Gardnerville, Nevada, is one of two areas where studies were begun in the mid-1970's to determine whether geochemically high concentrations of elements in the soil could cause changes in chlorophyll luminescence which could be detected with the FLD. Hemphill and others (1) and Watson and Hemphill (2) reported that increased molybdenum concentrations in the soil and plant ash caused marked reductions in the luminescence of juniper trees measured in July 1974 and May 1975. Luminescence intensities ranged from 0.2 ppb to more than 1.5 ppb rhodamine dye equivalency. The FLD was mounted in a helicopter during both tests and operated in a hover, nonimaging radiometer mode; each juniper tree tested either filled or nearly filled the FLD field of view during measurement.

Subsequent measurements made on June 5, 1978, with the imaging system depicted interesting luminescence patterns (fig. 3) but these patterns bore little or no correlation with molybdenum concentrations in the soil or plant ash. This lack of correlation was caused by a combination of relatively sparse vegetation in the test area and the coarse picture element size of the FLD in the imaging mode--about 45 m. Most of the area in each picture element was bare ground and represented a measure of luminescing constituents in the soil rather than in the juniper trees. However, figure 3 does show good correlation of luminescence shown on the FLD image and fluorite concentrations measured in soil samples collected along two traverses.

Several playas located in Torrance County, central New Mexico were imaged with the FLD in order to determine the distribution of luminescence intensity within and immediately surrounding the playas. Laboratory measurements of luminescence intensity of playa materials collected prior to the overflight showed values as high as 25 ppb rhodamine WT dye equivalence. The images were expected to provide a means of classifying components of the playa surface to guide future sampling, and a means of establishing an association between luminescence and chemical constituents.

Images were acquired on September 8, 1978 with the FLD operating at a wavelength of 589.0 nm. Five playas were overflown and all showed luminescence greater than expected. Parts of playa B, shown in red in figure 4, exhibit luminescence exceeding 90 ppb rhodamine WT equivalency, higher than playa C. Table 1 shows similar geochemistry for both playas, except for a substantially higher tungsten concentration in playa B. Tungsten is commonly associated with some geologic materials that luminesce, and may be the causative constituent for the higher luminescence in playa B. Striping in parts of the image shown in figure 4 is caused by periodic variation in the FLD automatic gain control and, as an instrument artifact, should be disregarded.

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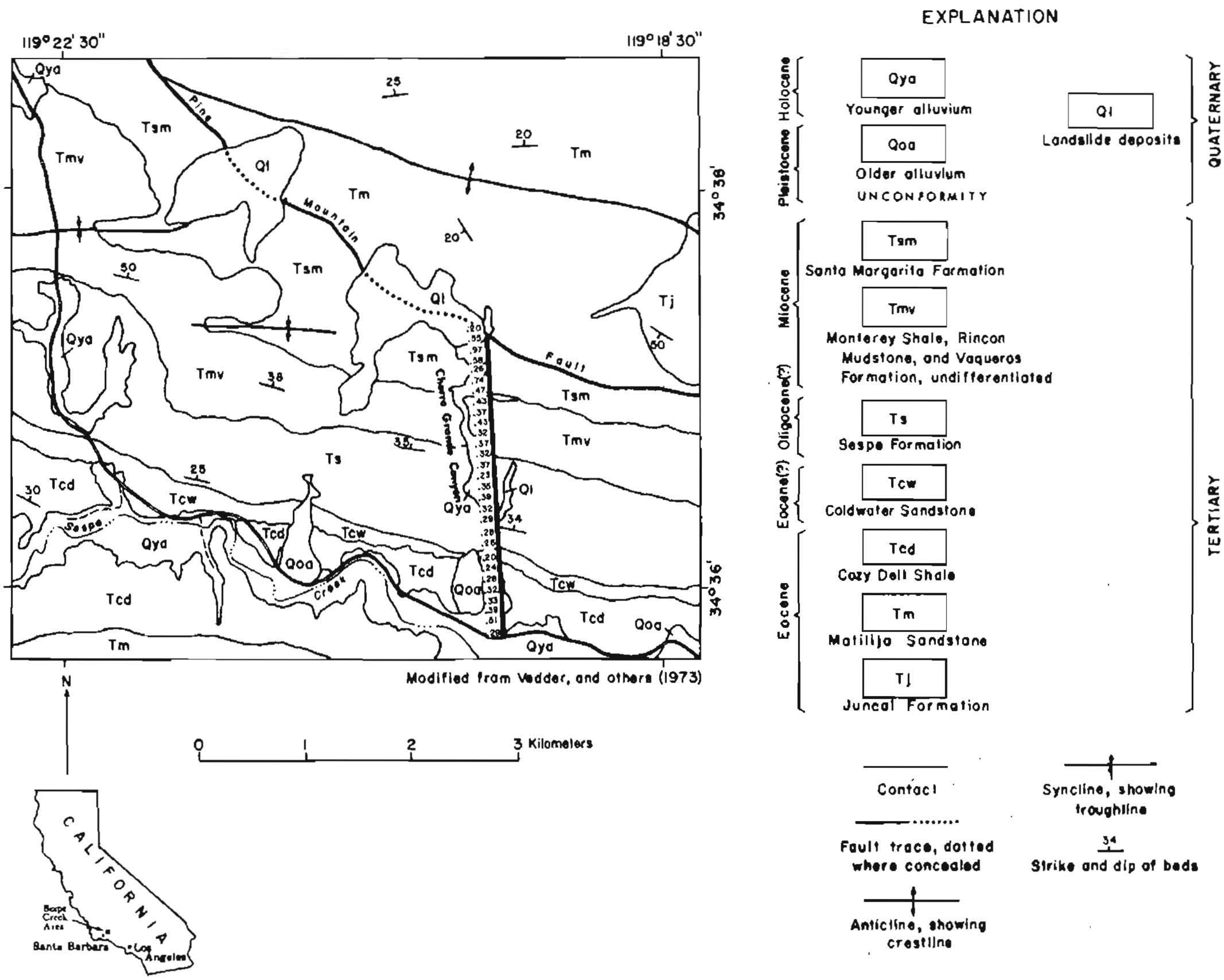

Figure 1. Geologic map of part of the Sespe Creek area, Ventura County, California, showing location of a helicopter traverse (solid line east of Chorro Grande Canyon). Numbers along traverse are FLD luminescence measurements in terms of rhodamine dye equivalency. Luminescence is markedly higher in the traverse segment across the outcrop of the phosphatic Santa Margarita Formation (Tsm).

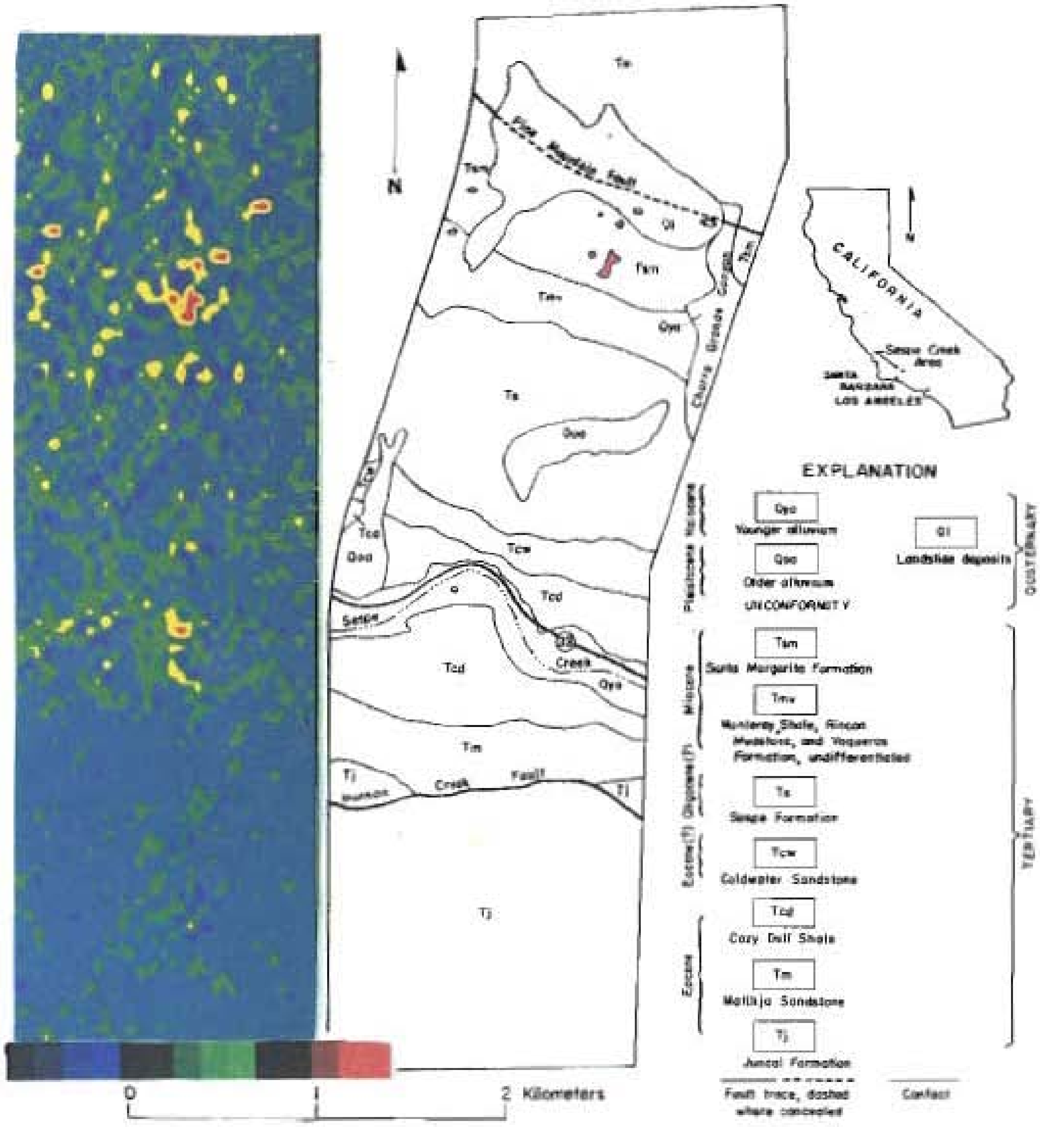

Figure 2. Luminescence image and geologic map of the Sespe Creek area, Ventura County, California. Image was acquired November 6, 1979, with the FLD imaging system operating at 486.1 nm. Red areas in both the image and the geologic map represent luminescence that exceeds 3.9 ppb rhodamine dye equivalency; luminescence highs correlate well with the occurrence of the phosphatic-gypsiferous Santa Margarita (Tsm) Formation. Lower luminescence is shown in the following colors: orange, 3.8-3.2; yellow, 3.1-2.2; green, 2.1-1.7; blue, 1.6-1.4; and dark blue, 1.3-0.1. Outline of the geologic map is modified to compensate for distortion in the image caused by aircraft roll and drift. (Geologic map modified from Vedder and others, (4).)

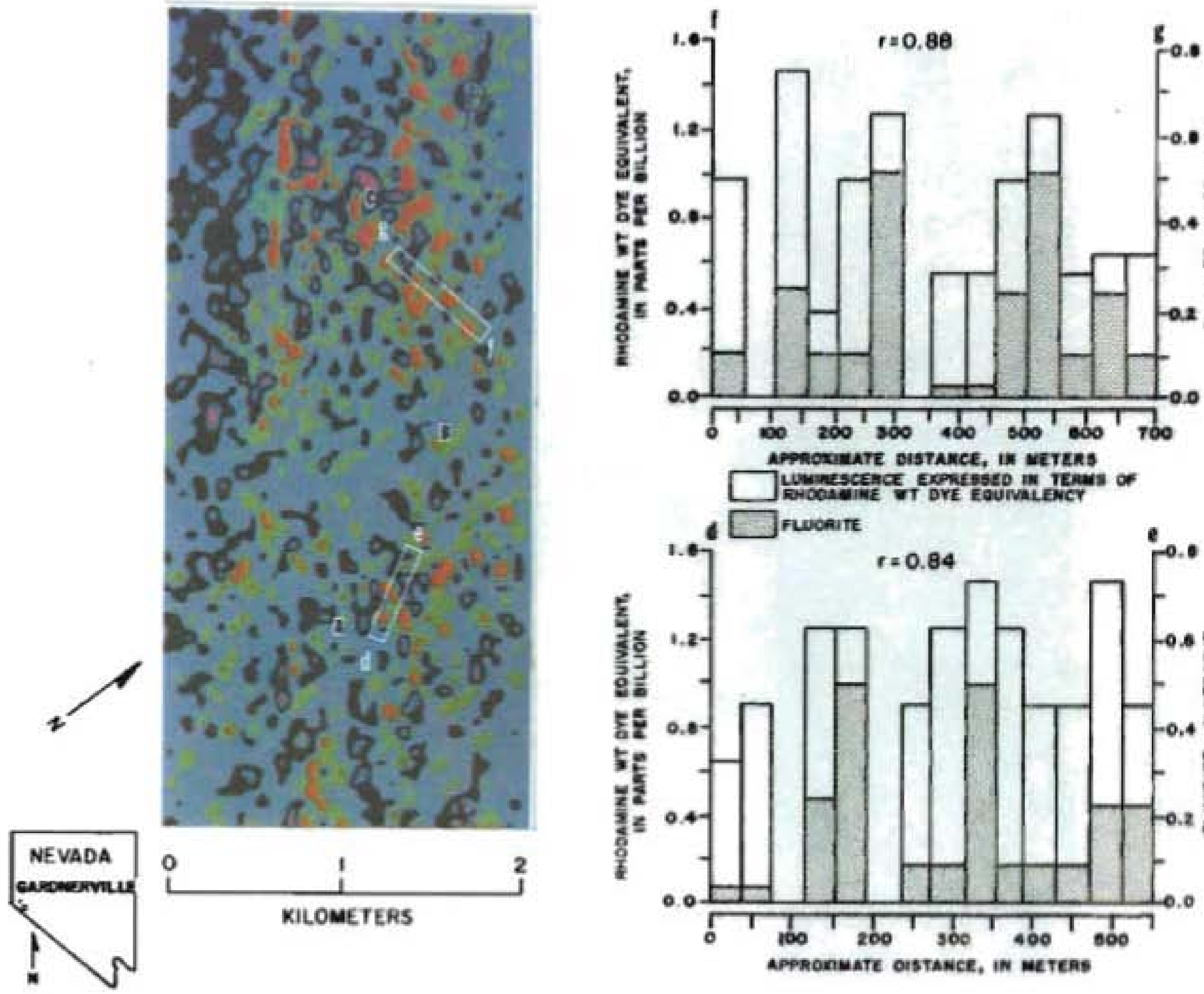

Figure 3. Luminescence image of the Pine Nut Mountain area, 17 km southeast of Gardnerville, Douglas County, Nevada, showing the location of Alpine Mill (A), Cherokee Mine (B), and the Divide Mine (C). Luminescence values, expressed as rhodamine dye equivalents, are shown in the following colors: violet, 0.00-0.22; blue, 0.23-0.51; very dark green, 0.52-0.61; purple, 0.62-0.66; light green, 0.67-1.15; orange, 1.16-1.36; and red, 1.37-1.50. Fluorite identified in soil samples on traverses d-e and f-g shows good correlation (r) at the 95 percent confidence level with luminescence measured using the FLD.

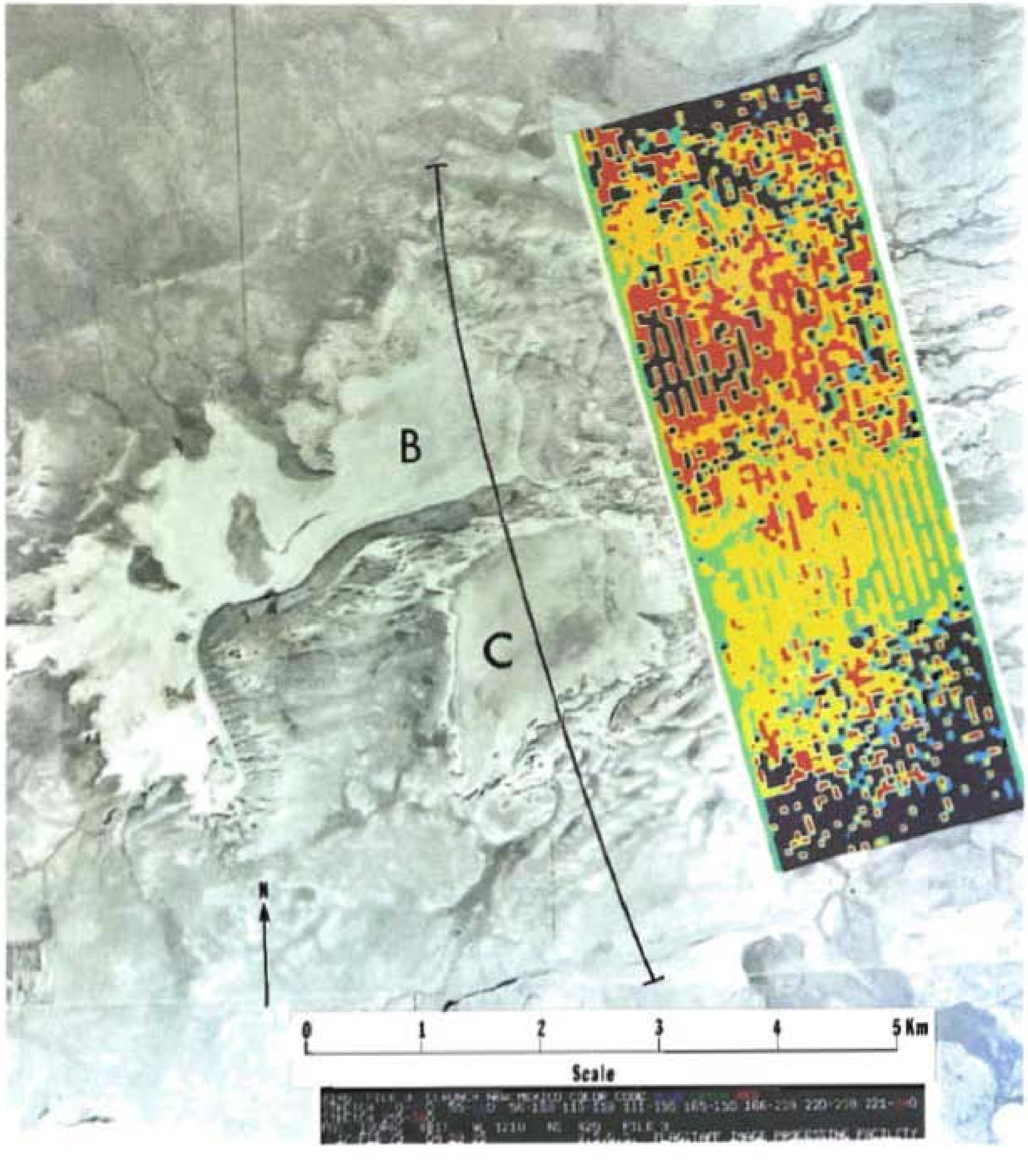

Figure 4. Aerial photograph and luminescence image of playas B and C about 25 km north of Corona, New Mexico. Solid line across the playas, shown on the photograph, is the ground trace of the aircraft flight line, and the approximate center line of the luminescence image. Red areas in the image represent luminescence that exceeds 90 ppb rhodamine dye equivalency, the highest luminescence intensity measured with the FLD.

Watson

Table 1. List of elements in parts per million for playas B and C, located in central New Mexico about 25 km north of Corona.

ELEMENTS	PLAYA B	PLAYA C
Ag	0.91	0.90
As	140.00	140.00
Cr	2.60	5.40
Li	62.00	61.00
Sr	910.00	1200.00
U	290.00	290.00
V	3.20	7.10
W	42.00	9.00
Ce	< 26.00	< 26.00
Pr	< 62.00	< 61.00
Nd	< 42.00	< 41.00
Sm	< 42.00	< 41.00
Eu	< 1.40	< 1.40
Gd	< 6.20	< 6.10
Tb	< 29.00	< 29.00
Dy	< 29.00	< 29.00
Er	< 9.10	< 9.00
Tm	< 4.20	< 4.10
Yb	0.14	0.20
Lu	< 20.00	< 20.00

APPLICATION OF FRAUNHOFER LUMINESCENCE TO OFFSHORE PETROLEUM EXPLORATION AND MARINE POLLUTION MONITORING,
Mitchell E. Henry, U.S. Geological Survey, Flagstaff, Ariz.

A series of experiments were designed to test the feasibility of using an imaging airborne Fraunhofer Line Discriminator (FLD) to detect, characterize, and map oils on a water surface. Laboratory measurements of luminescence of twenty-eight crude oils and thirteen commercially available refined products demonstrate a wide range in intensity of luminescence. Systematic differences occur between crude and refined products similar to those found by Riecker (1). When ratios of the values of luminescence measured at the 486.1 nm and 656.3 nm Fraunhofer lines are plotted (fig. 1), the two groups are effectively separated. With the exception of kerosene and commercial cleaning solvent, the ratios for refined products exceed 6 (6 to 442) and the ratios for crude oils are all less than 6 (0.7 to 5.2). With such a large range in values the natural logarithm of the luminescence values at 486.1 nm and 656.3 nm are plotted and yield a more interpretable figure (fig. 2).

In general, luminescence intensity increases at all emission wavelengths monitored (396.8 nm, 486.1 nm, 589.0 nm, 656.3 nm) with an associated increase in API gravity of the crude oils (figs. 3, 4, 5, and 6). Further, shifts occur both toward increasing luminescence intensity with decreasing wavelength among the aliphatic based crude oils when the 486.1 nm, 589.0 nm and 656.3 nm lines are considered and toward greater luminescence at 589.0 nm than at 486.1 nm in the aromatic based crude oils. Total luminescence measured at the 396.8 nm and 656.3 nm lines is typically much lower than that at the 486.1 nm or 589.0 nm lines for all crudes.

The ability to detect and discriminate among various slick forming pollutants with an airborne FLD requires data from at least two spectral bands. The dynamic nature of an oil film or other pollutant film on water is influenced by waves, winds, and currents, and therefore, requires the collection of synoptic multispectral FLD data.

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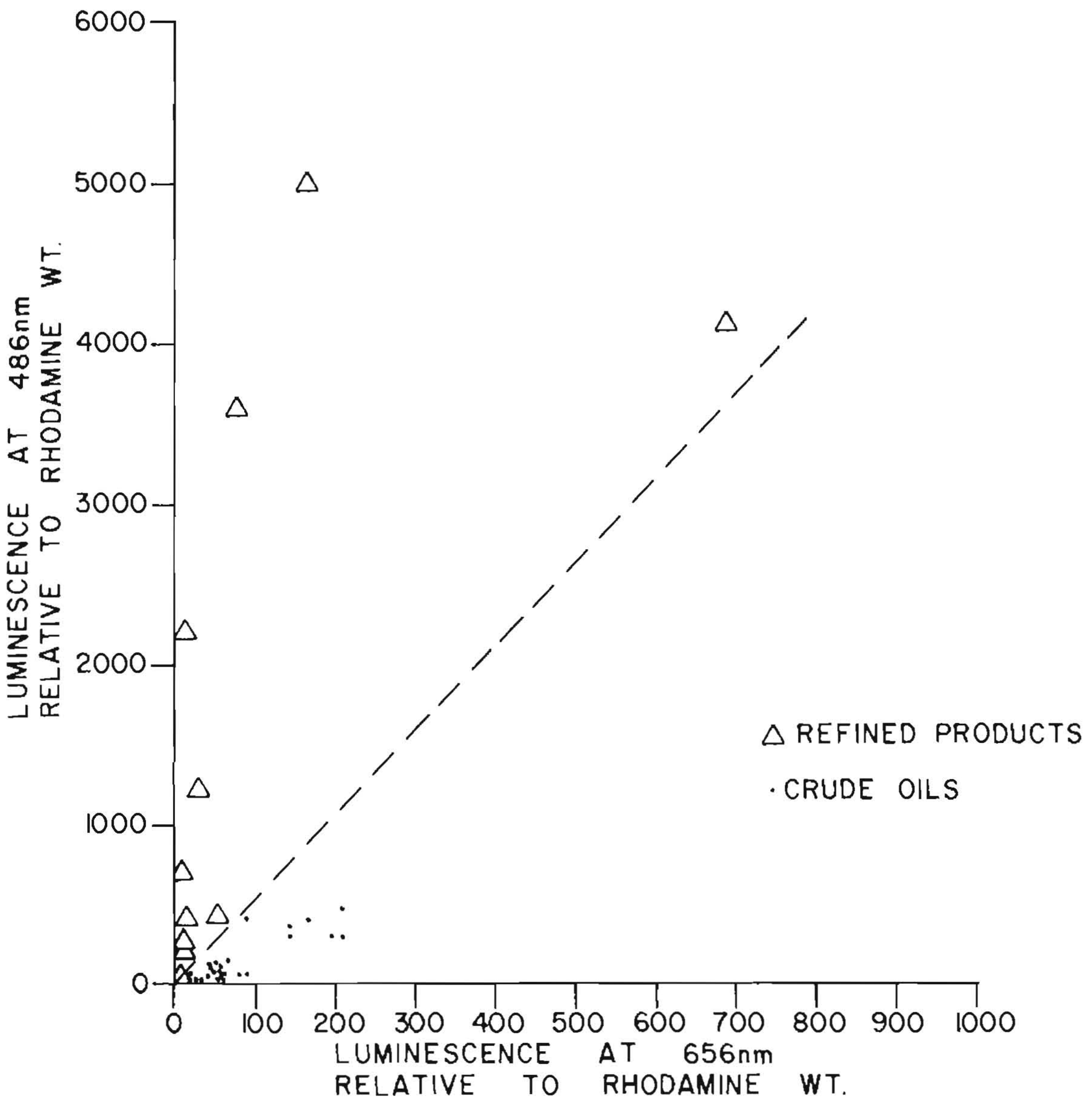

Figure 1. Luminescence intensity of crude oils and refined products at the 486 nm and 656 nm Fraunhofer dark lines (relative to rhodamine WT standard at 1200 ppb).

Mitchell E. Henry

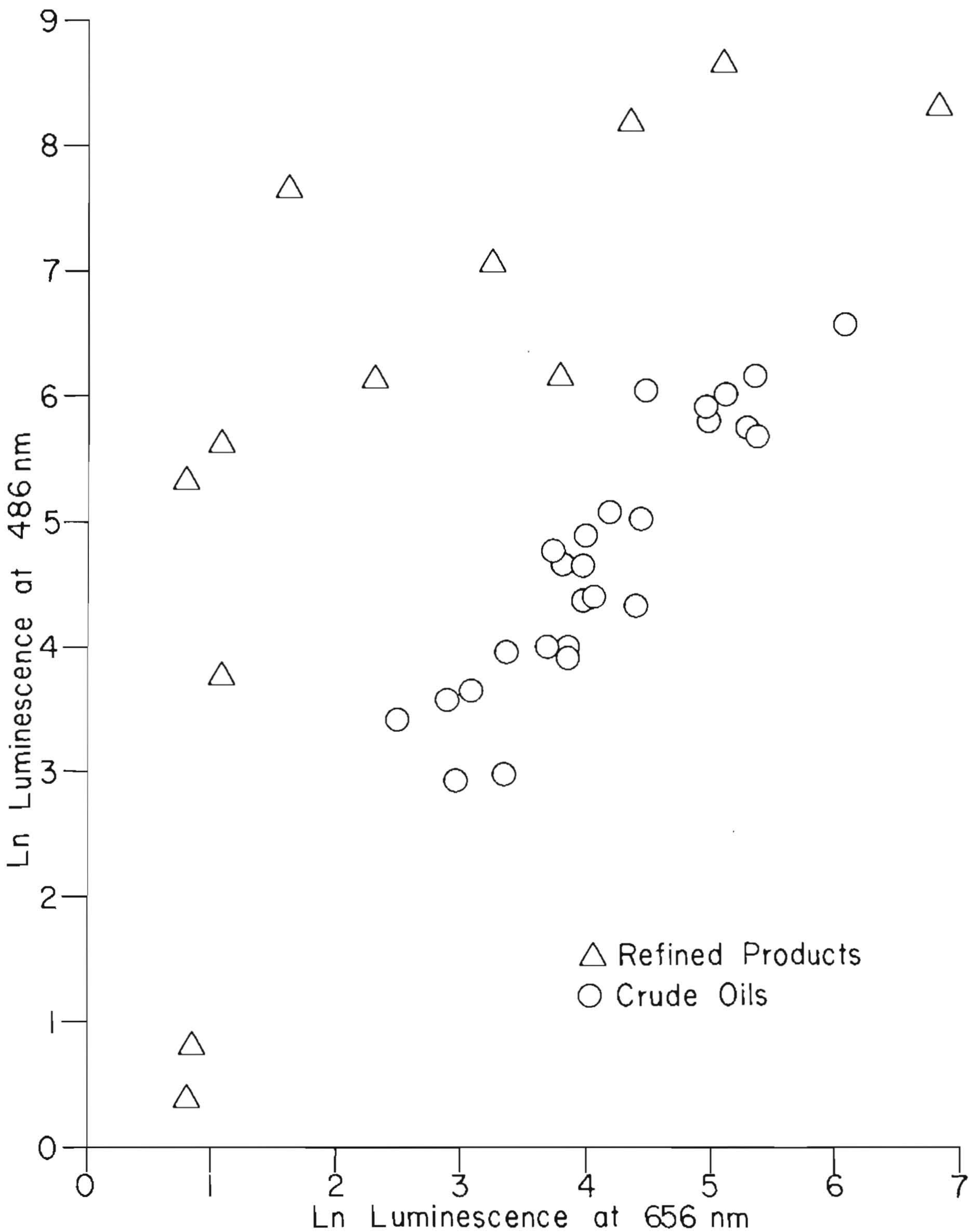

Figure 2. Logarithm of luminescence intensity of crude oils and refined products at the 486 nm and 656 nm Fraunhofer dark lines (relative to rhodamine WT standard at 1200 ppb).

Mitchell E. Henry

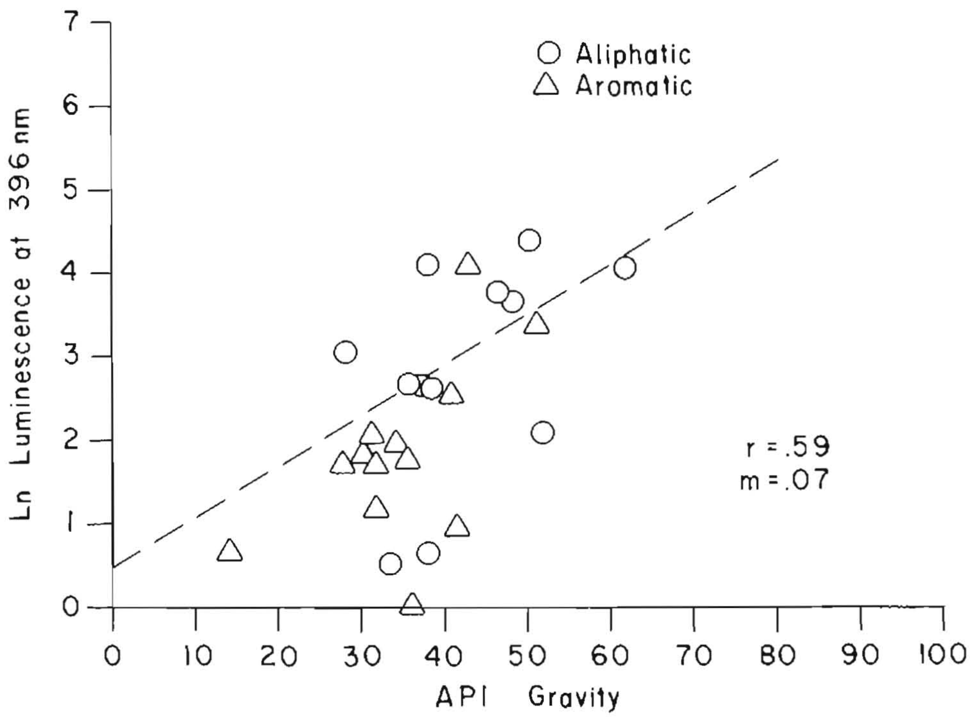

Figure 3. Logarithm of luminescence intensity of crude oils at the 396 nm Fraunhofer dark line (relative to rhodamine WT standard at 1200 ppb) plotted against API gravity.

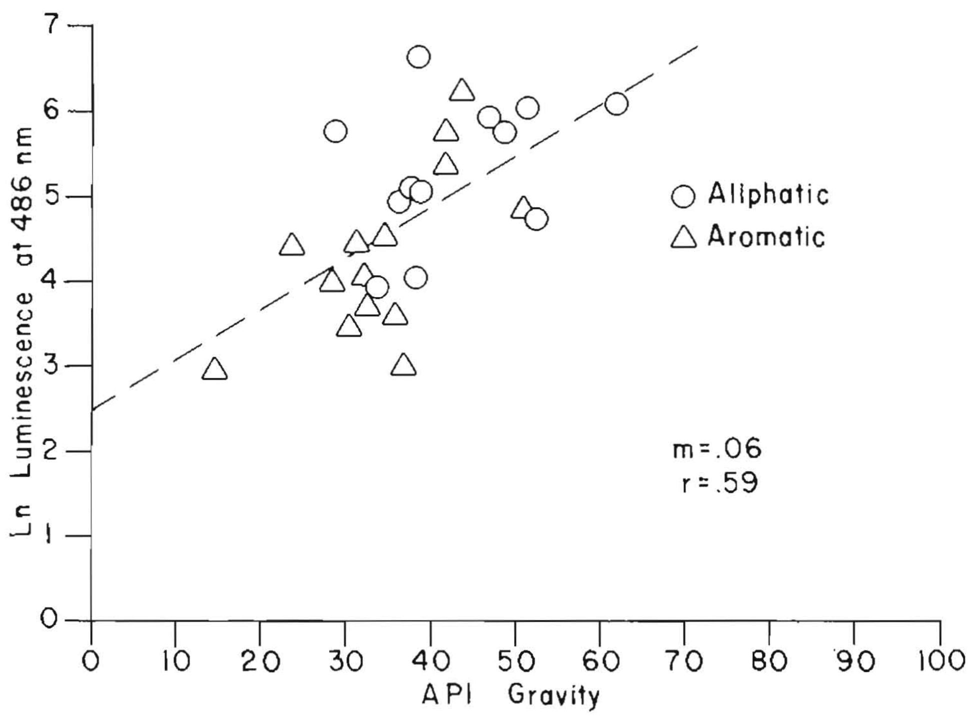

Figure 4. Logarithm of luminescence intensity of crude oils at the 486 nm Fraunhofer dark line (relative to rhodamine WT standard at 1200 ppb) plotted against API gravity.

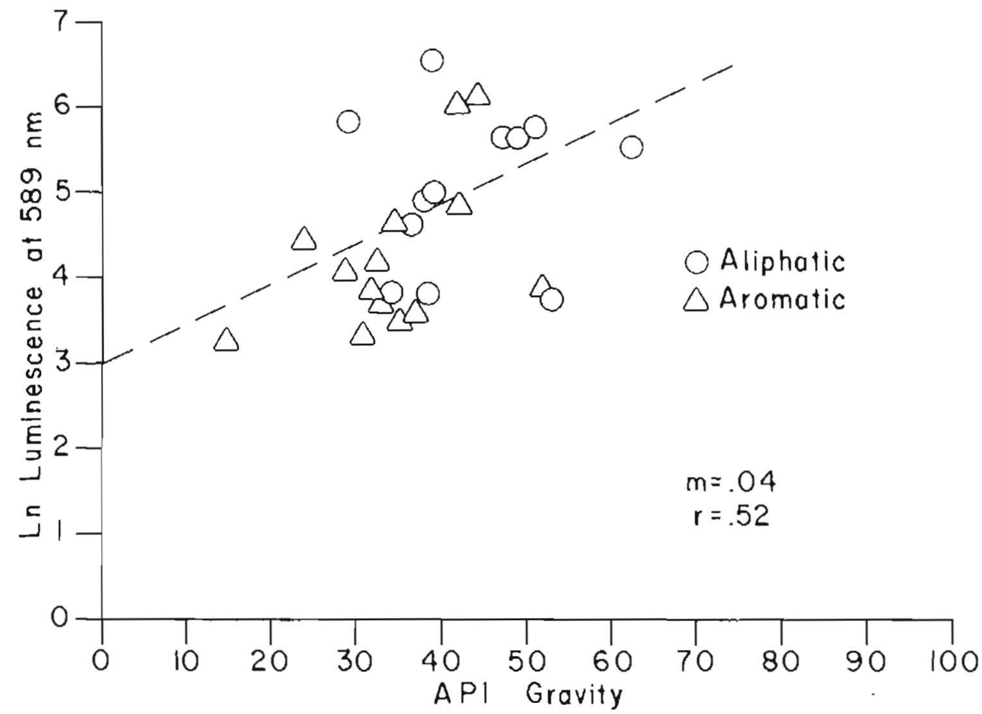

Figure 5. Logarithm of luminescence intensity of crude oils at the 589 nm Fraunhofer dark line (relative to rhodamine WT standard at 1200 ppb) plotted against API gravity.

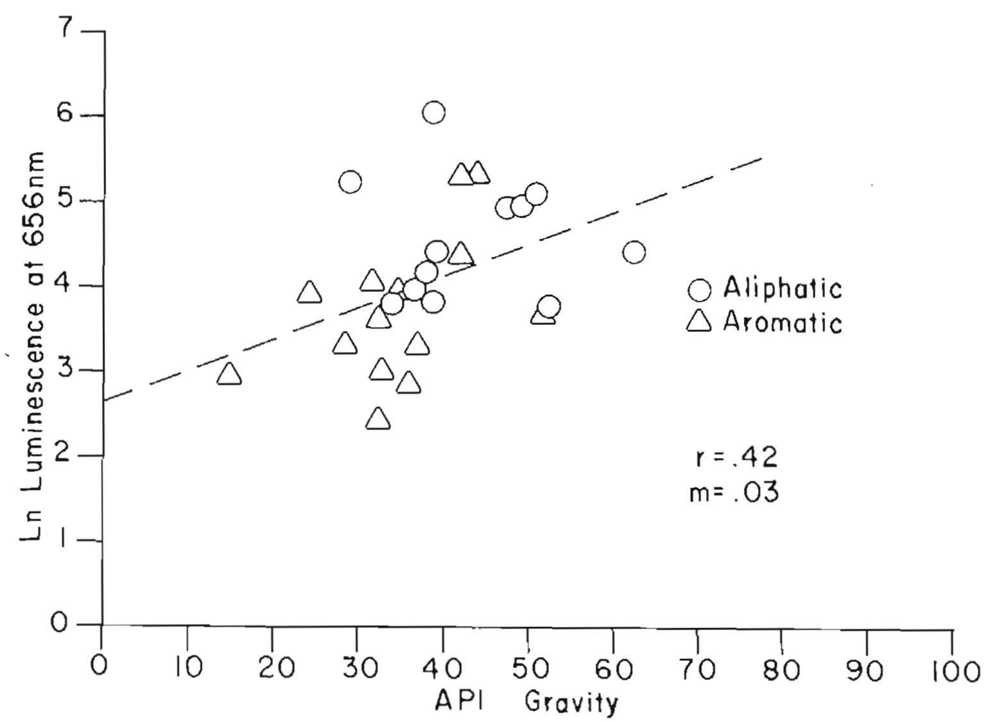

Figure 6. Logarithm of luminescence intensity of crude oils at the 656 nm Fraunhofer dark line (relative to rhodamine WT standard at 1200 ppb) plotted against API gravity.

AERIAL SURVEY OF LUMINESCENT ROCKS, BIG INDIAN VALLEY, UTAH,

Preston L. Niesen, Atlas Corporation, Moab, UT 84532

Images of luminescent rocks of Big Indian Valley, near Moab, Utah were acquired on June 12, 1978, with the airborne Fraunhofer Line Discriminator (FLD) imaging system operating at a wave length of 589.0 nanometers (nm). These measurements showed anomalously high values, as much as 3.08 parts per billion (ppb) rhodamine WT dye equivalence. Field and laboratory studies confirmed that high luminescence values are associated with areas of uranium-vanadium and copper mineralization. Laboratory spectrometer measurement of luminescence of rock samples also shows that the highest values of luminescence occur in rocks from which uranium and vanadium are produced. Luminescence at the 486.1 nm Fraunhofer line exceeds luminescence at 589. 0 nm, but clouds at the time of the overflight with the FLD precluded measurement of luminescence at 486.1 nm.

Five sites in Big Indian Valley having high luminescence values on the FLD image (Fig. 1) were ground checked for mineralization, and rock or soil samples were collected at each site. These samples were analysed for eleven major elements and eight trace elements. Results of these analyses are summarized in Table 1. A multiple linear regression analysis between sample luminescence and the 19 elemental analyses shows a good correlation between uranium content and luminescence. Other elements that appear to correlate with the luminescence of the laboratory samples are nickel, lanthanum, and vanadium. Zinc, cobalt and chromium were found to have a negative correlation with luminescence.

This preliminary experiment with an airborne FLD system shows that this approach can be used for at least some kinds of mineral exploration, and that development of a higher spacial resolution, multiple wavelength imaging system would markedly increase the usefulness of the FLD.

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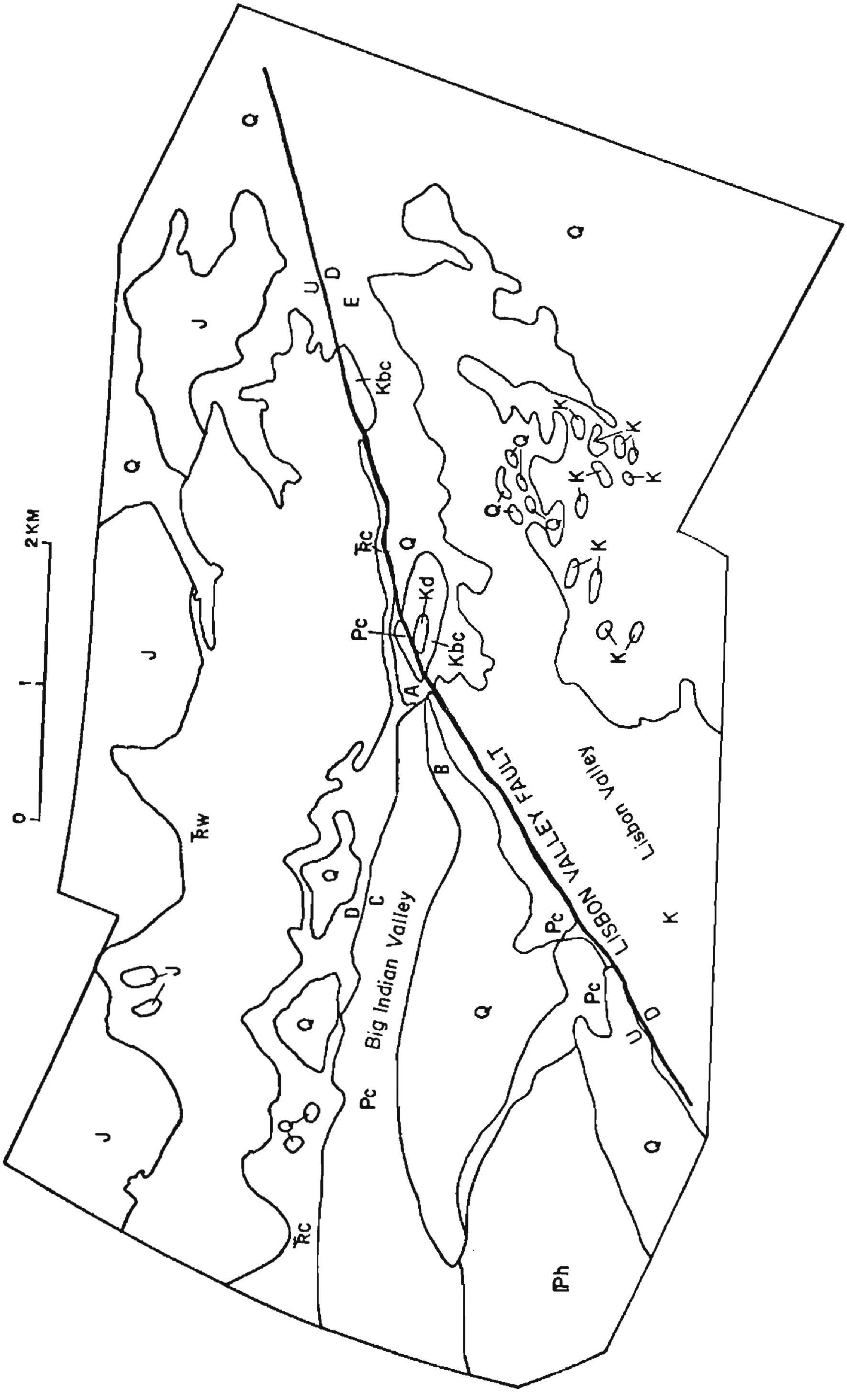

Figure 1a.--Map showing geology and locations of high values of luminescence, Big Indian Valley, Utah. Adapted from preliminary maps prepared by Wier and others (1, 2, and 3).

Niesen, P. L.

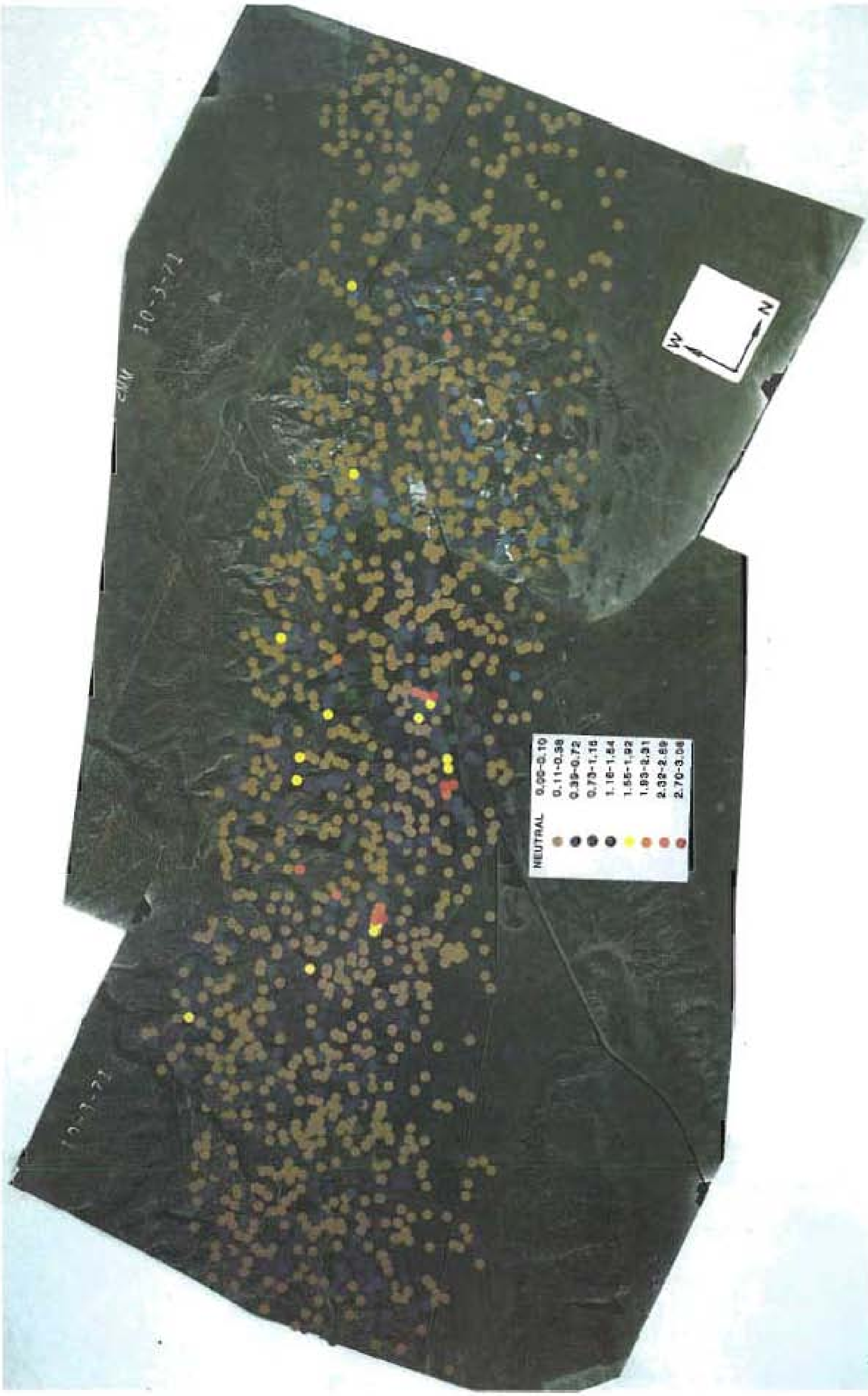

Figure 1b.--Aerial photograph mosaic of area shown in Figure 1a. Color dots show range of luminescence values measured with the FLD.

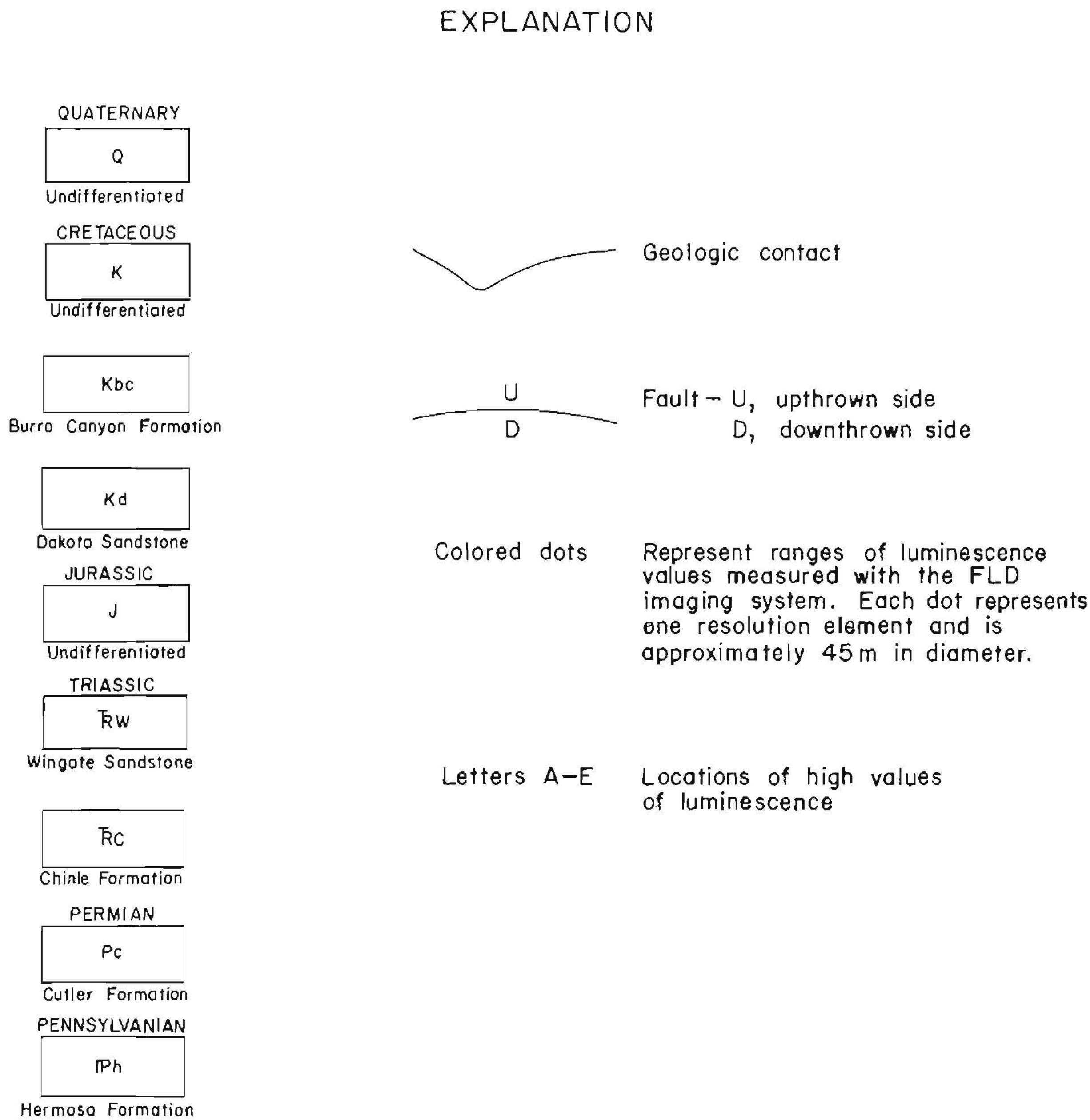

Figure 1c.--Explanation of map and aerial photograph mosaic shown in Figures 1a and 1b.

Niesen, P. L.

TABLE 1

Summary of Laboratory Analysis and Measurements

Luminescence of ground samples at 589.0 nm. (ppb rhodamine WT equivalence)	Site A (1.04)	Site B (0.98)	Site C (2.77)	Site D (0.80)	Site E (1.27)
Major elements (wt %)					
SiO_2	78.04	57.80	56.80	46.10	63.03
Al_2O_3	7.45	3.70	7.66	9.76	14.80
Fe_2O_3	1.88	0.95	1.94	3.54	3.58
MgO	0.64	1.18	3.77	2.63	1.25
CaO	1.99	18.02	11.21	17.28	3.78
Na_2O	0.01	0.29	0.58	0.48	5.89
K_2O	1.26	1.83	1.88	2.57	2.21
TiO_2	0.23	0.21	0.43	0.48	0.35
MnO	0.07	0.05	0.06	0.18	0.04
P_2O_5	0.13	0.19	0.10	0.21	0.17
LoI	5.80	13.86	13.04	15.00	3.42
Trace elements (ppm)					
Ni	7	30	24	28	6
Zn	40	17	30	37	22
Cu	4207	32	21	19	116
Co	8	4	45	14	5
La	23	14	57	39	39
Cr	17	49	45	14	17
V	49	44	72	66	74
U	31	43	910	40	30

Site A: Mean values of 16 samples collected at Big Indian Copper mine dump.

Site B: Mean values of 3 samples collected from an outcrop of Cutler Sandstone.

Site C: Mean values of 3 samples collected from the Small Fry mine dump.

Site D: Outcrop of Moss Back Member of the Chinle Formation.

Site E: Stream drainage from area of active and inactive uranium.

MEASUREMENTS OF SHOCK-INDUCED LUMINESCENCE AT METEOR CRATER, ARIZONA, FROM LABORATORY AND AIRBORNE FRAUNHOFER LINE-DISCRIMINATOR SYSTEMS. David J. Roddy, Robert D. Watson, and Arnold Theisen, U.S. Geological Survey, Flagstaff, AZ 86001.

A series of laboratory measurements has been completed on the impact-shocked sandstone and dolomite at Meteor Crater (Barringer Meteorite Crater), Arizona, to determine: (1) if the solar spectrum induces natural luminescence, and (2) if a correlation exists between intensity of luminescence and the degree of shock metamorphism observed in the rock. A series of airborne measurements also were made with the Fraunhofer Line-Depth (FLD) Method, using direct solar radiation as the excitation source, to determine if this remote-sensing technique can be used to detect and map the distribution of the most highly shocked rocks exposed at Meteor Crater. Preliminary results of both the laboratory and aerial measurements indicate that natural luminescence does exist and that it correlates with the intensity of shock in the Coconino Sandstone.

Natural luminescence in these rocks is related to a number of different types of transient and permanent deformations produced by the passage of high-pressure shock waves. One specific effect that has been identified is the shock wave production of internal defects that are sensitive to activation by electromagnetic energy in the visual and thermal wavelengths. For example, previous studies at Meteor Crater (1) and other impact sites (2,3) have demonstrated that shocked sandstone, limestone, and dolomite respond strongly to thermal excitation (15°C to 450°C) and release thermoluminescent energy. A comparable response in natural luminesence for shocked terrestrial rocks excited by the visible solar spectrum, however, had not been determined previously.

The technique used in airborne measurements involves the Fraunhofer Line-Depth (FLD) Method. Fraunhofer lines are very narrow wavelength regions in the solar spectrum which are caused by selective absorption of light by gases in the relatively cooler upper part of the solar atmosphere. The widths of Fraunhofer lines range from less than 0.01 nm to several tenths of a nanometer, and the central intensity of some lines is less than 10% of the adjacent continuum. The spectral positions of the lines are sharpest, deepest, and most numerous in the near-ultraviolet, visible, and near-infrared regions of the solar spectrum.

The FLD method of measuring luminescence involves measuring the ratio of the intensity of a Fraunhofer line with respect to the adjacent solar continuum. A second measurement of the identical FLD ratio reflected from the test specimen is also made at the same wavelengths. If no additional light is generated in the specimen to reduce the depth of the reflected line, such as by internal luminescence, the Fraunhofer line ratios are equal. If the reflected ratio is greater than the incident ratio, however, then a contribution from an internal luminescent component can be identified as having been excited for emission. Differences in reflectivity between the central intensity of a Fraunhofer line and the adjacent continuum can generally be ignored because variations of reflectivity with wavelength are negligible for most materials over a few nanometers in wavelength.

Figures 1-4 show the basic relations, described in detail in (4), that are in our FLD measurements. The instrumentation used for these measurements is described by Hemphill and Watson in (4), and consists of a Perkin-Elmer engineered model FLD designed for NASA's Advanced Application Flight Experiments (AAFE) Program. The FLD system used for the airborne remote sensing consists of an optical head and an electronic console for continuous recording and real-time onboard playback. The main components in the optical head are two telescopes (one earth-looking and one sky-looking); a rotating optical chopper wheel; three replaceable optical filter sets for three Fraunhofer lines; and a photomultiplier with its power supply. A standard lamp, simulating sunlight and skylight, illuminated the sky-looking telescope. The earth-looking telescope observed the target whose reflectivity and luminescence were to be measured. Light from the two telescopes was sequentially routed through two different paths by the rotating chopper wheel. In one path, light passed through a filter that was centered at a specific Fraunhofer line. This signal constituted the light intensity measured on the solar continuum adjacent to and including the Fraunhofer line. In the other path, a Fabry-Perot interference filter, with half-width of less than 0.07 nm, passed light coincident with the intensity of the central part of the Fraunhofer line. These signals were fed to a mini computer that generated luminescence and reflectance data by solving the appropriate equations. Three sets of Fabry-Perot filters were available, permitting measurements of Fraunhofer wavelengths at 656.3, 589.0, and 486.1 nm.

The laboratory measurements were made with a Perkin-Elmer MPF3 fluorescence spectrometer that provided a source detector and solar-corrected solar spectrum for comparison with the same wavelength regions measured by the airborne system. Laboratory measurements were made on a variety of samples from each of the different rock types at Meteor Crater, the local surface soils, surrounding vegetation, and caliche-coated rocks. Without exception, the most highly shocked samples of Coconino Sandstone from the southern ejecta blanket exhibit high levels of luminescence, 10 to 65 times as great as unshocked background material. High levels of luminescence were measured also in the shocked sandstone from the excavated shaft debris of glass and Coconino fragments on the crater floor and excavated Coconino ejecta on the north rim. The qualitative correlation of luminescence from the Coconino Sandstone with shock metamorphism in these rocks indicates a positive contribution from shock-induced luminescence.

The area covered by the airborne FLD measurements incorporates about 4 km^2 surrounding the crater. The FLD instrument had a ground resolution of ~ 45m viewed from a flight altitude of ~ 2500 m AGL and 90 knots forward ground speed. Results are identical with the laboratory measurements, i.e. the only locations that luminescence strongly are the three locations described above and shown in Figure 5. These three areas are strongly luminescent because they are relatively freshly excavated exposures of the most highly shocked Coconino rocks. A thin surface cover of soil, windblown material, and alluvium blankets most of the area and prevents airborne observations of the larger region of shocked ejecta.

Preliminary results indicate that solar light does indeed stimulate the shocked sandstone and that a direct correlation exists between the most highly shocked material in the ejecta blanket and the level of intensity of luminescence excited by the visible solar spectrum. The second objective was to determine if solar-stimulated luminescence can be detected from the air using the Fraunhofer Line-Depth Method. This technique has proven to be feasible within the limits of erosional cover and the high resolution of the equipment. Since this airborne FLD system is capable of detecting luminescent materials in the parts-per-billion range (4), it would be appear useful to further outline limits of the technique to determine its feasibility in detecting scattered or isolated areas of shocked rocks in remote areas known to be impact sites. Specific mechanisms involved in the solar activation of luminescent defect sites in the crystalline lattices also require further study. A feasibility study of a solid-state imaging FLD from spacecraft is being completed by R. Watson and A. Theisen (U.S. Geological Survey). Preliminary calculations indicate that satellite detection of natural luminescence sensitivities comparable to current airborne FLD data are possible with ground resolutions of less than 40 m.

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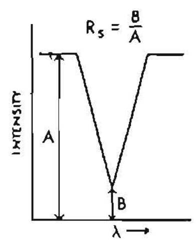
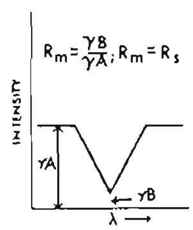
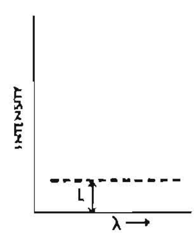


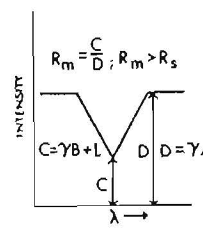
1. LINE PROFILE OBSERVED IN THE SOLAR SPECTRUM DIRECTLY



2. SOLAR LINE PROFILE REFLECTED FROM NON-LUMINESCING MATERIAL



3. LUMINESCENCE CONTRIBUTION



4. LINE PROFILE OF MATERIAL CONTAINING BOTH REFLECTED AND LUMINESCENT COMPONENTS

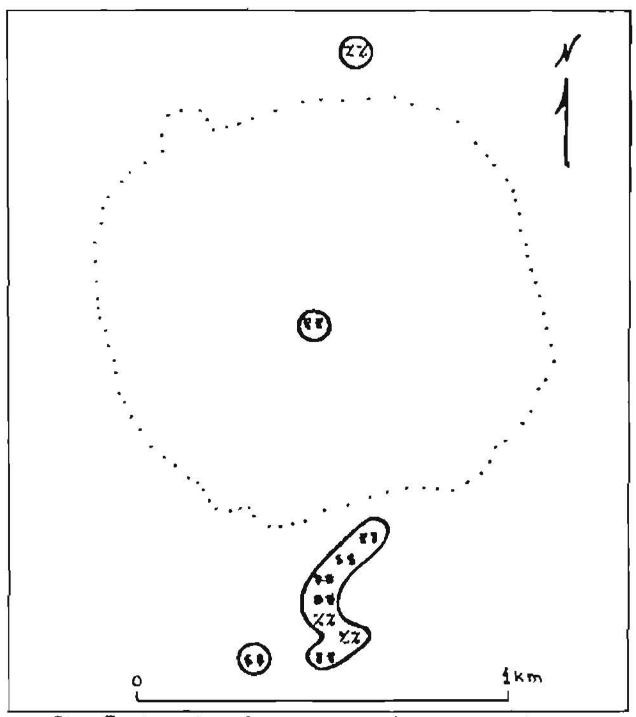


Fig. 5. Location of most intense luminescent sites detected by airborne Fraunhofer Line Discriminator System at Meteor Crater, Arizona. These areas of highest luminescence are schematically outlined by solid lines. The enclosed symbols are computer normalized maximum luminescent values. The dotted line marks the trace of the rim crest.

DIGITAL PROCESSING TECHNIQUES FOR SMALL DIGITAL ARRAYS (FLD DATA SET); Pat S. Chavez, Jr., Robert D. Watson, Mitchell E. Henry, and Arnold F. Theisen, U. S. Geological Survey, Flagstaff, AZ 86001

The Fraunhofer Line Discriminator (FLD), an airborne, remote-sensing instrument for measuring luminescence, has been used since 1977 to successfully image formations of such materials as oil seeps, geochemically affected vegetation, and uranium-bearing sandstones (1). Detailed descriptions of the Fraunhofer Line Depth method for measuring luminescence and a description of the FLD imaging system that collected the data used in this project are available in the literature (1 and 2). The system was originally designed to operate as a non-imaging radiometer with an instantaneous field of view of one-degree, and a frequency bandwidth of 40 Hertz. When the system was converted to operate in an imaging mode it was limited to measuring only 36 points or pixels per sweep, at one sweep per second.

Because the array is so small the FLD image must first be enlarged or expanded if the data is to be used for visual interpretation. Because there are only 36 pixels per scan line the results given by enlarging the image optically in the photo lab is not acceptable for interpretation because of the pixel size. Therefore, the image must first be expanded digitally by increasing the size of the digital array. There are several methods that can be used to enlarge digital arrays (i.e., pixel duplication, cubic spline, etc.). We wanted a method that would give satisfactory results for visual interpretation and minimize the amount of computer time required to do the expansion. The results of pixel duplication, which is the fastest method to use, are blocky and difficult to interpret (see figure 1). The computer time needed for higher order interpolation techniques was more than what we wanted to use. As a compromise we used a two-dimensional spatial filtering technique to smooth the digital array after it was expanded by pixel duplication. The enlargement factor used was eleven, so each pixel was duplicated into an array of 11 by 11 elements. Two different window sizes were then used in the spatial filtering program to smooth the enlarged digital array. The first window size used was a square of eleven pixels and it was selected because it would smooth the enlarged digital array and leave the center pixel brightness unchanged. This allowed us to smooth the data and keep the brightness statistics close to the original values.

The second window size used to process the expanded array was a 5 by 5 rectangle. This filter was applied twice to the data in order to eliminate some of the blocky patterns. It was not used more than twice because we wanted the brightness statistics of the image to be as close as possible to the original FLD image. The results of the two different filter sizes were compared, and the single 11 by 11 filter size seemed to be the better one in our case. The two 5 by 5 filters smoothed the data more gradually, but it did not smooth the data enough.

The images of two areas, San Barbara Channel, California, and Pinenut Mountains, Nevada were used in the study. The results of the pixel duplication and smoothing filters for the Pinenut Mountains are shown in figure 1.

Single variable data sets are often shown only in a black and white format. Because the human eye can easily see at least one order of magnitude more color differences than shades of grey, it is to the advantage of the interpreter to use some of the well known color-coding techniques to display a single variable set of data. In our case two different methods were used to color-code the FLD image. The first method was a simple technique familiar to most interpreters. It maps specific digital numbers or brightness ranges in the image to a selected color and is often referred to as "color-density slicing". This technique works well if there are not too many distinct levels to be separated. The interpreter must be careful when using the product made with this technique because brightness boundaries can easily be exaggerated or introduced into the image.

To solve this problem and increase the number of different brightness levels that can be seen a continuous color-coding technique was also used. This is similar to using a linear contrast stretch except that the brightness levels are shown in color. The relationship of bright to dark grey values is preserved and can be used by the interpreter. This information can be lost with the first method discussed above. To code a single variable set of data over a continuous color range the values are contrast stretched so that the lower range of values are mapped to blue, with a gradual transition to red for the higher values. The blue, green, and red components needed to color composite the data into a continuous color range are made by applying three different contrast stretches to the same set of data. Two different ways to stretch the set of data for continuous color-coding are shown in figure 2. Due to the format of this publication no color prints are shown.

The choice of which color-coding technique should be used in the image interpretation depends primarily upon the features that require emphasis (i. e., broad patterns or fine detail separation). In some applications, perhaps both techniques need to be considered.

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Chavez, Pat S., Jr., et. al.

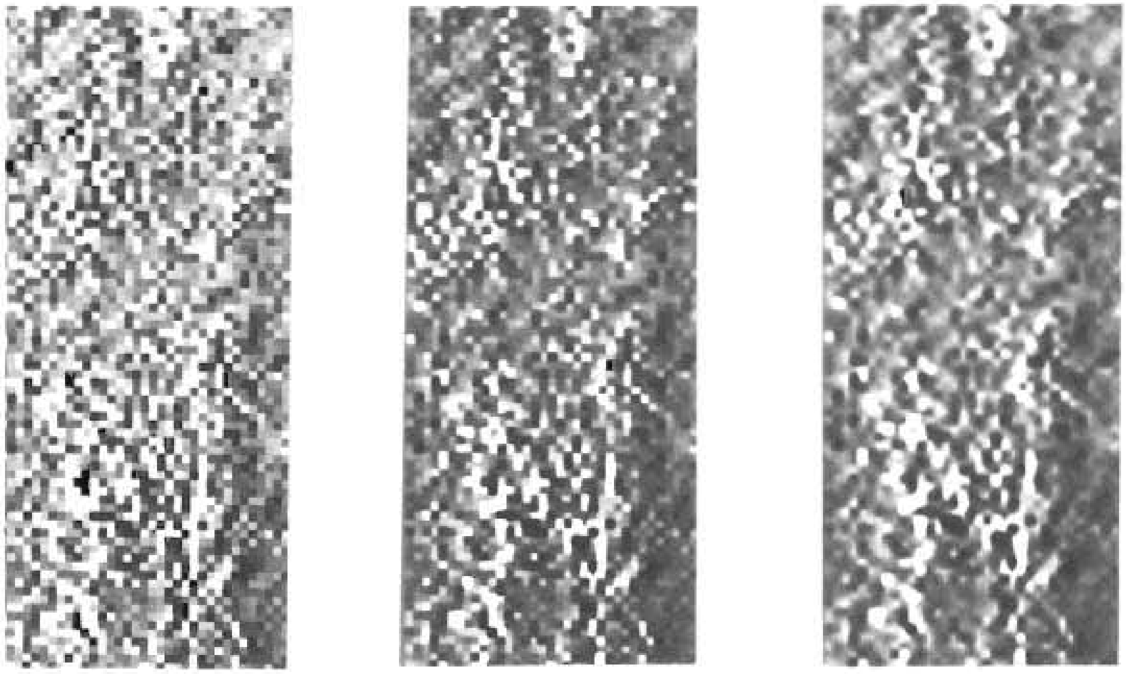

Figure 1.--The left photo shows the original FLD image after an 11 by 11 digital enlargement using pixel duplication. The middle photo is the result of two 5 by 5 smoothing filters applied to the original image on the left. The photo on the right is the result of a single 11 by 11 smoothing filter applied to the photo on the left.

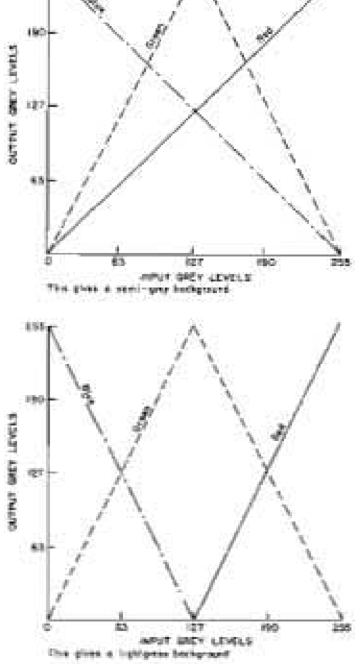

Figure 2.--The plots above show two possible ways that a single variable or monochromatic image can be stretched to generate blue, green, and red plates for color-coding the data into a continuous color spectrum.

NEW DESIGN FOR AN IMAGING FRAUNHOFER LINE DISCRIMINATOR,
Philip N. Slater, University of Arizona, Tucson, Arizona

Previous designs for an imaging Fraunhofer line discriminator (1, 2) have not very satisfactorily met the requirement for constant spectral bandpass with change in field angle. The reason is that the wavelength position of the passband of any Fabry-Perot filter depends on the incidence angle to the filter. Moreover, the narrower the passband, the more sensitive the system is to variations in the angle of incidence.

A telecentric system with an array of Fabry-Perot filters was suggested by Plascyk (1). A difficulty with this approach is that the telecentric portion of the system has to be large to adequately reduce the variation in the angles of incidence across the filters. The solution presented by Slater (2), of using a fan-shaped array of narrow field systems to cover the whole field, suffers the drawback of large size and inevitably some residual nonuniformity of spectral response across the field.

The approach presented here utilizes the fact that the Fabry-Perot filter acts as an angle as well as a wavelength filter. Thus, a given narrow wavelength interval will be transmitted by the filter at successive angular increments when the optical path difference through the filter is such as to produce constructive interference. The interference fringe pattern, owing to an extended area source at infinity, produced by a focusing lens placed behind the filter, is a series of concentric rings described by the equation

$$p\lambda = 2nd\cos\theta$$

where

p, an integer, is the order of interference,
λ is the wavelength of interest,
n is the refractive index of the filter spacer layer,
d is the geometrical thickness of the spacer layer,
θ is the angle of incidence to the filter.

A constant spectral passband over a given field of view can thus be obtained by operating a filtered imaging system in a pushbroom mode, as shown in Figure 1. The flux entering the system at 8.5° to the optical axis is sampled over a 120° arc in the image plane by a CCD detector array. A fiber optics sheet transforms the arc image to a line so that readily available linear single arrays of CCDs or CCD linear arrays in the time delay and integration (TDI) mode can be used.

There are several advantages to this imaging geometry. First, the imaging system is uniangular, covering a ring centered on the optical axis, having a width typically less than 1 mrad. This means that the image-forming system can be designed to be diffraction-limited. Second, the angular line of sight is constant, minimizing angular variations in sensing ground radiances. Third, all the radiant flux contributing to the image traverses the same distance through the atmosphere. This means that the atmospheric transmittance is the same for each image point although there will still be variations in atmospheric path radiance.

Some readers will recognize the similarity between this uniangular pushbroom scan geometry and the conical scan geometry of the S192 experiment on Skylab. There is an important distinction between the two, however, which should not be overlooked. The conical scan on S192 was achieved by mechanical means. The image was scanned over a single detector in each band, which meant there was a delay between the recording of the start and end of a scan line. With inadequate attitude stabilization, scan positional errors can be introduced in the across-track direction, giving rise to image reconstruction and registration problems. In the uniangular pushbroom mode, detectors cover the whole field of view and the image is sampled electronically. The entire image arc is sampled simultaneously, so no positional errors can be introduced across a single arc image.

The calculation of the first-order relationship between system parameters and performance proceeds as follows: First, the angle to nadir is determined for the chosen altitude and swath width. Second, the angular width of the Fabry-Perot ring corresponding to this angle to nadir and for the required spectral resolving power is found. Third, the focal length of the imaging system is calculated to make the Fabry-Perot ring width equal to the detector dimension in that direction. The geometrical projection of the detector size onto the ground gives the ground IFOV. Fourth, for the calculated focal length and for a chosen fast imaging system (F/1.2 was used in the cases examined here), the size of the Fabry-Perot filter is determined. Finally, the sensitivity of the system in parts per billion (ppb) of rhodamine WT dye is calculated for assumed values of integration time and the noise equivalent exposure (NEE) of the CCD array. For example, for a swath width of 60 km and an altitude of 700 km we see from Figure 2 that the ground IFOV is about 540 m and the 3σ sensitivity is about 0.6 ppb. Figure 3 shows the parameter-performance relationships for the case of a 185-km swath. Note that for a given altitude the ring width is finer, which means that the IFOV is smaller but which in turn means that the integration time is smaller, resulting in a less sensitive system.

In the preceding preliminary calculations the system MTF was taken as unity. The result of taking system MTF into account, using the EIFOV concept (2) is shown in Tables 1 and 2 for the cases of an aircraft and an orbital system. In these cases the focal lengths have been chosen to provide nine stages of TDI to improve the system SNR by a factor of 3. Note that the swath width in the case of the aircraft has been restricted to 200 m, simply to gain sensitivity by using a smaller angle to nadir and thereby a larger ring width. The main problem with regard to the aircraft is that, for the flight conditions preferred by the U. S. Geological Survey, the velocity-to-height ratio is 2.5 times that for the orbital system. This proportionally reduces the integration time and the system sensitivity. The system compactness, however, should make it simple to arrange several systems in a fan to provide wide swath coverage.

Finally, as Tables 1 and 2 show, the systems are practically identical in angular field and focal length. This means that the same system could be used for a shuttle flight and in an aircraft program. The only minor change required would be to sum groups of detectors together in the across-track direction for the aircraft system.

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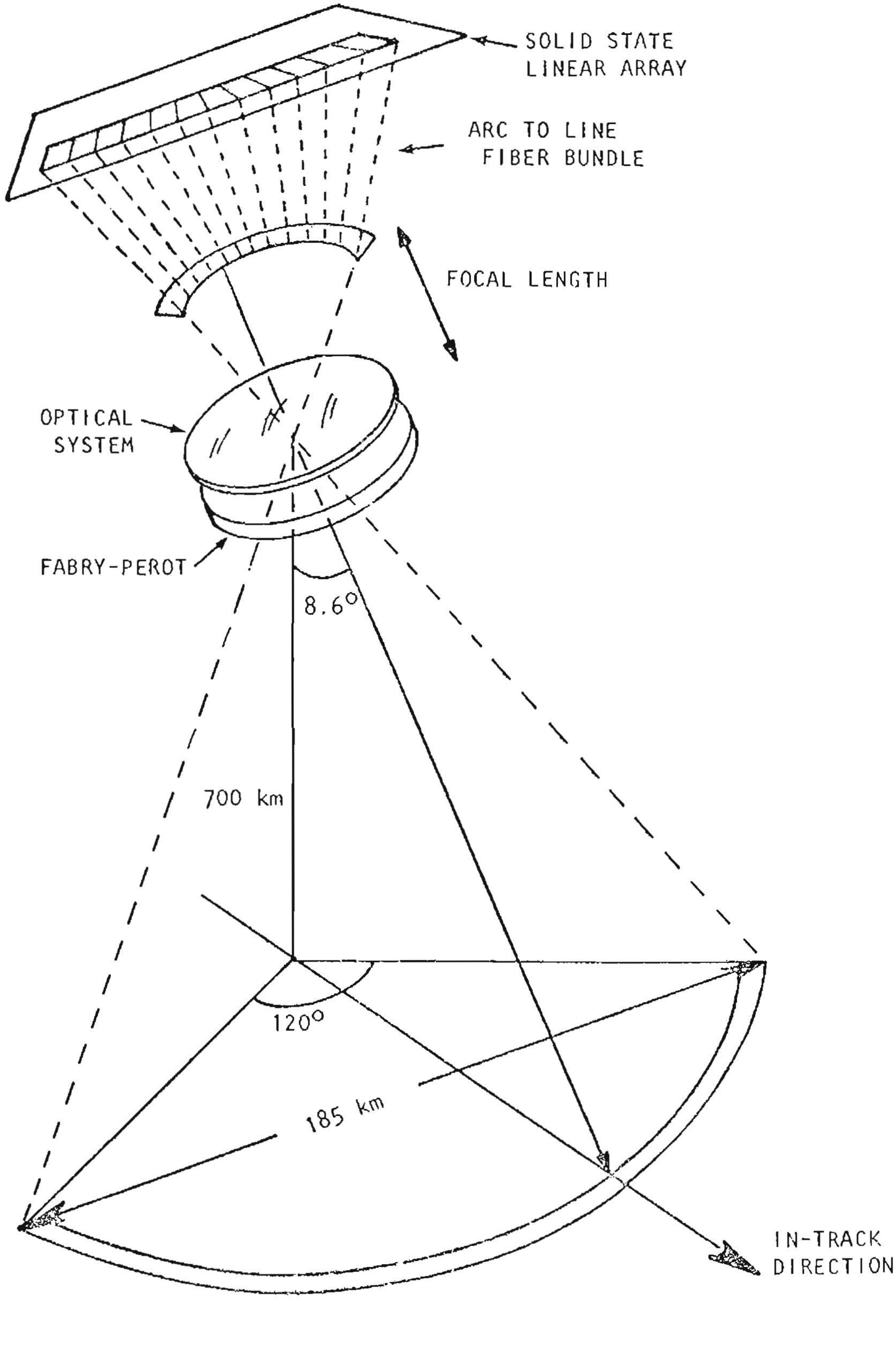

Fig. 1. Uniangular pushbroom imager using a Fabry-Perot and a solid-state linear array.

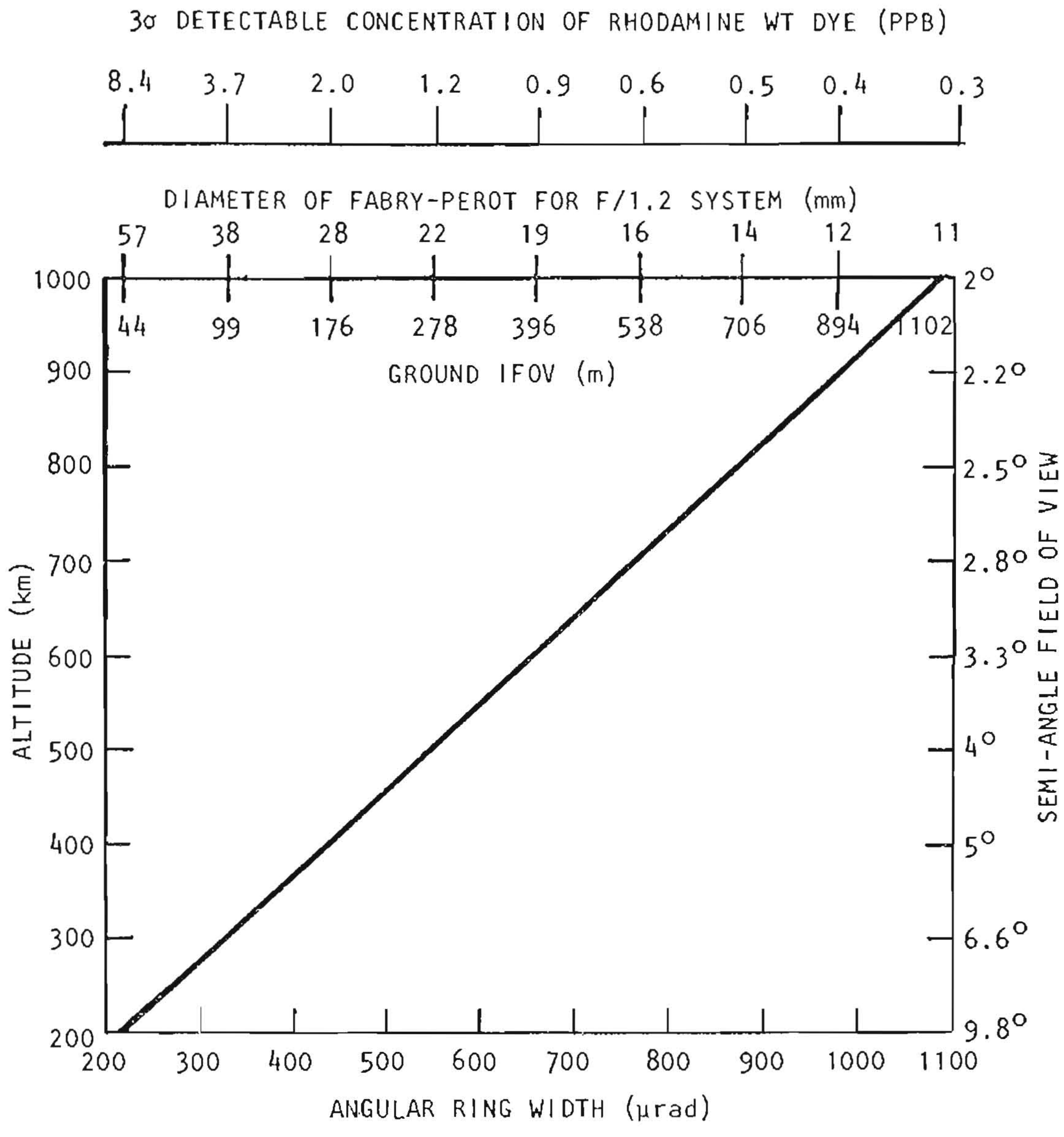

Fig. 2. Parametric relationships for systems with 15-μm arrays and image smear for a swath width of 60 km and a spectral resolution of 0.025 nm.

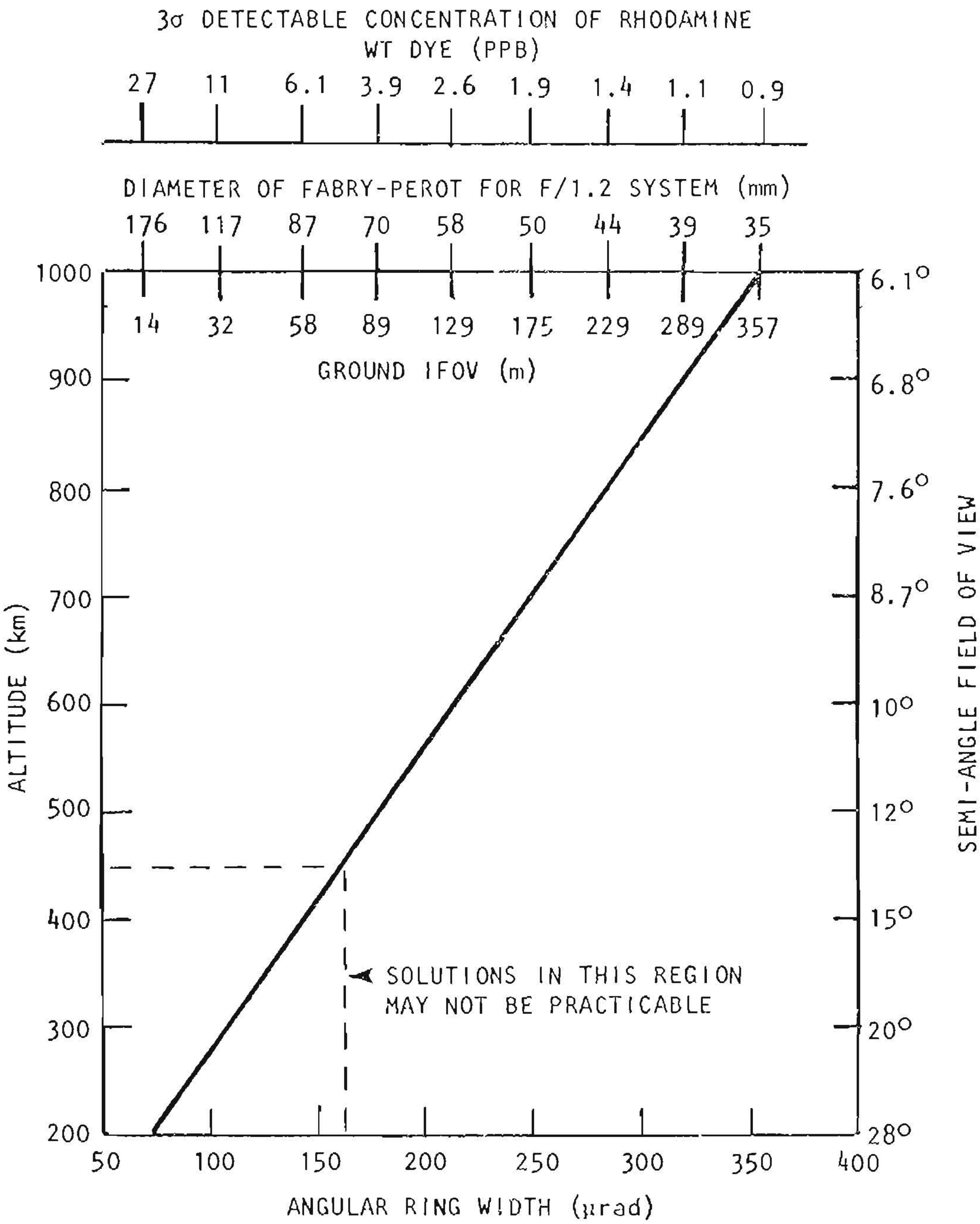

Fig. 3. Parametric relationships for systems with 15-μm arrays and image smear for a swath width of 185 km and a spectral resolution of 0.025 nm.

Table 1. FIRST-ORDER SOLUTION FOR AIRCRAFT SYSTEM

ALTITUDE	2,400 m
SWATH WIDTH PER SYSTEM	200 m
GROUND VELOCITY	50 $m \cdot s^{-1}$
F-NUMBER	1.2
FOCAL LENGTH	170 mm
FIELD ANGLE	2.76°
DETECTOR SIZE	15 x 15 μm
INTEGRATION TIME	4 ms
NOISE EQUIVALENT EXPOSURE	10^{-7} $J \cdot m^{-2}$
WAVELENGTH	656 nm
HALFWIDTH OF PASSBAND	0.025 nm
SOLAR IRRADIANCE IN PASSBAND	0.044 $W \cdot m^{-2}$
ATMOSPHERIC TRANSMITTANCE	0.8
BACKGROUND REFLECTANCE	0.1
NUMBER OF STAGES OF TDI	9
NUMBER OF DETECTORS SUMMED ACROSS TRACK	64
IFOV	13 m
3σ SENSITIVITY TO RHODAMINE WT DYE	0.5 ppb

Table 2. PARAMETERS AND PERFORMANCE FOR A POSSIBLE ORBITAL SYSTEM

ALTITUDE	700 km
SWATH WIDTH PER SYSTEM	60 km
GROUND VELOCITY	6.8 $km \cdot s^{-1}$
F-NUMBER	1.2
FOCAL LENGTH	180 mm
FIELD ANGLE	2.83°
DETECTOR SIZE	15 x 15 μm
INTEGRATION TIME	8.6 ms
NOISE EQUIVALENT EXPOSURE	10^{-7} $J \cdot m^{-2}$
WAVELENGTH	656 nm (H_α)
HALFWIDTH OF PASSBAND	0.025 nm
SOLAR IRRADIANCE IN PASSBAND	0.044 $W \cdot m^{-2}$
ATMOSPHERIC TRANSMITTANCE	0.8
BACKGROUND REFLECTANCE	0.1
NUMBER OF STAGES OF TDI	9
IN-TRACK EIFOV	72 m
ACROSS-TRACK EIFOV	56 m
3σ SENSITIVITY TO RHODAMINE WT DYE	2.8 ppb

THIRD-GENERATION FRAUNHOFER LINE DISCRIMINATOR FOR AIRBORNE AND SPACEBORNE REMOTE SENSING OF SOLAR-EXCITED LUMINESCENCE, Sherman K. Poultney, The Perkin-Elmer Corporation, Danbury, CT. 06810

Preliminary design concepts developed for third-generation Fraunhofer Line Discriminators (FLD) can meet new airborne and spaceborne requirements. These requirements include simultaneous operation at two or more Fraunhofer lines, 10-degree swath coverage, MK-II FLD-equivalent sensitivity, and appropriate spatial resolution (e.g. 200 m for spaceborne and 3 to 5 m for airborne).[1] The design concepts are based upon the proven principle and capabilities of the MK-II FLD built by Perkin-Elmer for the National Aeronautics and Space Administration and the U.S. Geological Survey.[2]

Six of the considered designs are summarized in Figures 1 and 2. The five design concepts in Figure 1 use the central airy fringe of the Fabry-Perot etalon. The area array options differ in the array architecture and electronic processing. The concept of the novel configuration FLD with along-track pushbroom is summarized[3] in Figure 2. Preliminary estimates show that the first concept is impractical, that the second two fall an order of magnitude short of the sensitivity goals, and that the last three can meet the requirements if the necessary subsystems can be realized.

The novel configuration FLD consists of a Fabry-Perot etalon and blocking filter, larger than the similar FLD-II optics, that form an image of at least the fringe with angular radius of 5 degrees for the Fraunhofer line being observed, and a pushbroom Charge-Coupled Device (CCD) array configured to lie along this fringe (see Figure 2). A second semicircle of array pixels at the appropriate fringe position inside the first allows view of the background outside the Fraunhofer line. This radiometer part of the novel configuration FLD can achieve the airborne requirements if all the necessary subsystems can be designed and built. Extension to a spaceborne version requires the angular resolution to be improved by a factor of 3 to 5, the number of detector elements to be increased similarly, and some means of signal improvement to be used to maintain sensitivity, one of which would be to utilize a larger Fabry-Perot interferometer (e.g. 30 cm diameter). Reynolds et al[4] have demonstrated interferometers similar to those required here.

Although several FLD design concepts can meet the new airborne and spaceborne requirements for luminescence sensing, the novel configuration FLD with along-track pushbroom scan appears to be particularly interesting. Perkin-Elmer plans to continue its considerations of the engineering feasibility of this and other FLD design concepts to support NASA and USGS programs.

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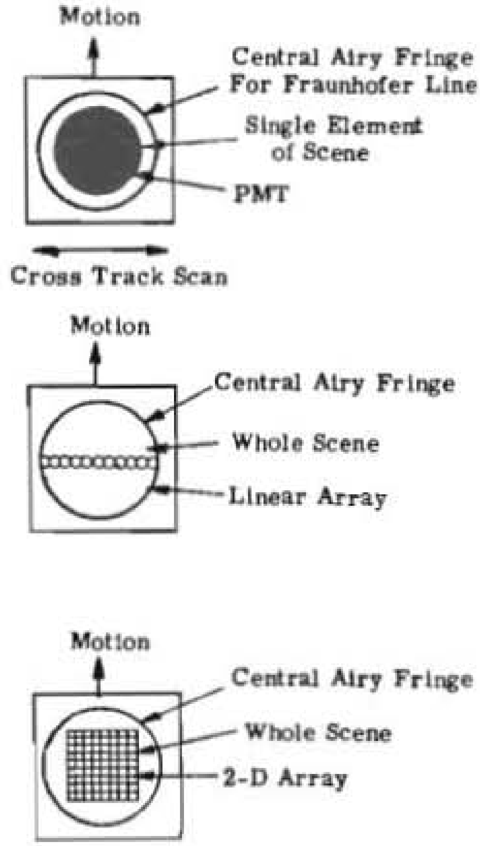
Sherman K. Poultney



1. Cross-Track Whiskbroom Scan With Single Element Detector
2. Along-Track Pushbroom Scan With Linear CCD Array
3. Fast Frame Staring Scan With Area Array
4. On-Chip TDI Staring Scan With TDI Array
5. Off-Chip TDI Staring Scan With CCD Area Array

Note: Each Concept Requires a Second Focal Plane to Detect the Same Scene Outside the Selected Fraunhofer Line.

Figure 1. Third-Generation FLD Design Concept Summary (Conventional Configuration)

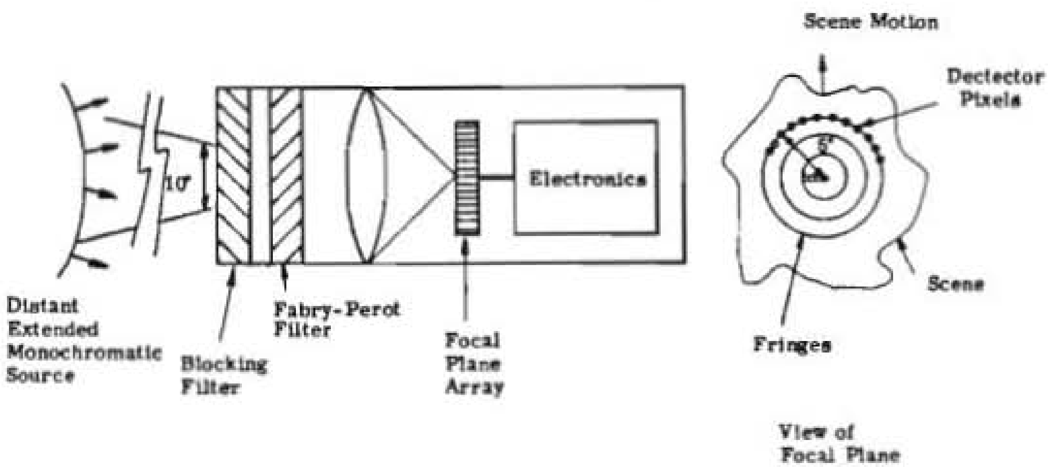


Figure 2. Basic Concept of Novel Configuration FLD with Along-Track Pushbroom Scan.

PROPOSED DESIGN FOR AN AIRCRAFT AND SPACE SHUTTLE COMPATIBLE FRAUNHOFER LINE DISCRIMINATOR,

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The Fraunhofer line discriminator (FLD) is a computing photometer operating in an imaging mode that determines and displays values of both luminescence and reflectance coefficients of scenes within the instrument's field of view. The FLD has demonstrated the capability of detecting luminescence at levels of less than 0.2 parts per billion (ppb) rhodamine WT dye equivalence[1/] from an aircraft altitude of 2,380 m above terrain and at an instantaneous ground resolution of 45 m. The design objective for an improved aircraft and space compatible FLD would be to detect minimum levels of rhodamine WT equivalence of 0.10 ppb at a spacial resolution of 3 m from an aircraft altitude of 3 km and 200 m from a shuttle altitude of 200 km. In addition, the FLD system should be simple in design, yet sufficiently flexible to permit simultaneous operation at more than one Fraunhofer wavelength.

A detailed photometric analysis of the FLD (1) demonstrates the potential feasibility of using the FLD technique from an orbiting platform. Detection of 40 ppb rhodamine dye at a ground resolution of 1.6 km would require a 4.3 cm objective telecentric telescope. A collector objective of 98 cm would be required to achieve a ground resolution to 0.16 km. These figures are not compatible with the design objectives quoted above and require that a somewhat different systems approach be taken to increase sensitivity and improve ground resolution.

An image-intensified solid-state charge coupled device (IICCD) imaging system can be designed to satisfy the requirement for high resolution and sensitivity. In addition, charge coupled device (CCD) arrays produce excellent image quality when dealing with extremely low contrast scenes (2) and, because of the large dynamic range of CCD's, permit sophisticated postmission signal processing.

The use of multielement arrays also permits the concept of time delay and integration (TDI) to be applied. TDI requires that each element in an array column views the same resolution area on the ground sequentially, and cascades its charge additively to the next element in the column (3). The signal to noise ratio is therefore increased by the square root of the number of elements in a column.

Applying both the IICCD and TDI concepts to the design of a third generation FLD results in a dramatic improvement in signal to noise ratio, compared to standard photodiode arrays, and enables design objectives to be achieved. For example, using a 30 cm objective telecentric system, 16 stages of TDI, and a gain of 1,000 for a IICCD detector, results in a minimum detectable RMS luminescence (L) of

$$L = 2.80 \times 10^{-4} \quad (486.1 \text{ nm})$$

$$3.10 \times 10^{-4} \quad (589.0 \text{ nm}) \text{ and}$$

$$2.70 \times 10^{-4} \quad (656.3 \text{ nm})$$

1/ A description of rhodamine dye equivalency is contained in "Quantification of luminescence intensity in terms of a rhodamine WT standard" by Watson, R. D., these proceedings.

for a shuttle orbit altitude of 200 km and a ground resolution of 200 m. Using the relationship between rhodamine WT dye concentration and luminescence as measured with the second generation FLD (i.e., $L = 10^{-2} \times C$) and 3-sigma values of luminescence, results in a minimum detectable rhodamine WT dye equivalency of

$$C = .083 \text{ ppb } (486.1 \text{ nm})$$

$$.075 \text{ ppb } (589.0 \text{ nm}) \text{ and}$$

$$.080 \text{ ppb } (656.3 \text{ nm}).$$

The above calculations also included a 0.25 reduction in optical system throughput to permit operation at two Fraunhofer wavelengths simultaneously. This would be accomplished by using dual beam splitters to permit viewing of the ground scene in the solar continuum and Fraunhofer line for two Fraunhofer wavelengths simultaneously. Ratioing of Fraunhofer luminescence signals from pairs of Fraunhofer lines will be possible, therein normalizing the effects of the atmosphere and improving the capability of the system to identify specific materials. Modest modification of the optical system also will permit operation from light aircraft with spatial resolution of 3 m from an altitude of 3 km.

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A CORRELATION SPECTROMETER APPROACH TO DESIGN OF AN FLD,
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The principal interferent in the space-borne measurement of earth luminescence is the flux from atmospheric scattering and surface reflectance, which can be 200 times the luminescence flux and vary in space and time by at least a factor of 3. However, the luminescence can be discriminated because it is spectrally "smooth", while the scatter is modulated by the Fraunhofer spectrum, which is constant in space and time.

If the upward flux is measured as a in the continuum and b at the center of a line of strength k, then

$$a = \alpha (F+B) \quad b = \beta (F+kB) \tag{1}$$

where F and B are the luminescence and scattered photon spectral exitances and α and β throughputs (i.e. collecting area x f.o.v. x efficiency x spectral bandwidth).

From (1)

$$F = ((k\beta/\alpha)a-b)/\beta(k-1) \tag{2}$$

and, in the shot noise limit, with $Bk >> F$, $(k)^{\frac{1}{2}} << 1$ and $\beta = 1$ the maximum S/N for a 1 second measurement is $F/(Bk)^{\frac{1}{2}}$ when $\alpha = k^{\frac{1}{2}}$.

Now consider a group of m lines of comparable strengths ki in a region where B may be assumed independent of wavelength. Then the measurements

$$e = \gamma (F+B) \quad f = \beta (mF+Bk) \tag{3}$$

give $F = ((K\beta/\gamma)e-f)/\beta(k-m) \quad (k=\sum ki)$ (4)

and $S/N = mF/(BK)^{\frac{1}{2}}$ (5)

If ki = k the improvement is $m^{\frac{1}{2}}$ and in general is $m(k/K)^{\frac{1}{2}}$ which is >1 if $(K-k) < (m^2-1)$.

By increasing the number of measurements, other interferents can be rejected including simple polynominal dependence of B on wavelength.

Dick, R.

Multiple matched spectral filters of this type are used in the BRL COSPEC instruments for the measurement of atmospheric SO_2 and NO_2, where the absorption band spectrum is discriminated from a variable background. In COSPEC, the filters are realized (1), (2) by multiple slit masks placed sequentially in the focal plane of a spectrometer.

Because of the narrowness of the Fraunhofer lines, a COSPEC FLD would require careful optical design to fold the required long focal lengths into a measurable volume. Also, even with the multiplex advantage it would be difficult to equal the throughput of an F-P type filter. In compensation, there could be improved interferent rejection, operation at wavelengths other than the major Fraunhofer lines, ease of changing wavelength and possible operation as a push broom imager.

For an order of magnitude estimate of sensitivity, consider an f/6 0.5 meter spectrometer with a 1200 ℓ/mm grating and 1 cm high slits operating on the lines at 430.8, 432.5, 434 and 438.3 nm which would give $m = 4$, $K \sim 2$ and a bandwidth of 0.53 mm

With a spectral slit width of 0.07 to 0.1 nm, an optical efficiency of 0.1, PMT quantum efficiency 0.1, and taking B = 2.5E12 photons/cm^2sec sterad A, equation (5) gives S/N = 1 for F = 3E8 photons/cm^2sec sterad A or an S/N of about 30:1 for 0.1 ppb Rhodamine equivalent. However, this is the theoretical limit, instrumental stability and the necessity of accounting for spectral variations of B and other interferents could substantially increase the minimum detectable luminescence.

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ATMOSPHERIC EFFECTS IN THE REMOTE MEASUREMENT OF THE LUMINESCENCE OF EARTH MATERIALS

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Introduction

The atmosphere affects the measurement of surface luminescence from space,
(a) by adding to the received flux via elastic and inelastic scattering of sunlight and the fluorescence of trace species.
(b) by reducing the luminescent flux through scattering and absorption.
(c) by altering the downward flux which excites the luminescence.
All of these effects vary in time and space and with wavelength.

Additive effects

Table 1 lists the most likely additive effects with estimates of their contributions to the total flux. The elastic scattering albedo is by far the largest contributor and, while it is the interferent most easily rejected by the Fraunhofer Line Discriminator, it determines the photon noise, which is the ultimate limit to measurement of luminescence.

The values in Table 1 are for the region of the Sodium D_2 Fraunhofer line at 590 nm, chosen because it exhibits all the significant effects and is the most extensively studied, due to its interest to aeronomists.

Other possible airglow interferences are listed in Table 2; there appears to be a lack of data on the daytime intensities of these emissions.

The flux estimates of Table 1, which are tentative only, (perhaps within a factor of 3) were derived as follows. The elastic albedo is based on the charts of ref. (1) for midsummer, mid-latitude, with a surface reflectance of 0.25 and a visual range of 14 km. The line centre depth of the D_2 line is based on the profiles in (2) and (3).

The nitrogen Raman flux is based on the cross-section given by Rosen (4), a scale height of 8 km and the sea level flux of (5).

The aerosol fluorescence was estimated from (6), where Birnbaum equates the fluorescence from typical L.A. aerosol to that from 2 ppm of NO_2, combined with the ratio, given by Fouche et al (7), of 116:1 between NO_2 fluorescence (per nm, at 488 um) and N_2 Raman, per mole at S.T.P.

The pump intensity for aerosol fluorescence was taken (arbitrarily) to be the same as for NO_2 and was obtained by multiplying the solar spectral flux by a low resolution absorption spectrum of NO_2.

The Na dayglow flux is from (8) with a resonable assumption as to the background sky brightness under the conditions of these experiments.

The Ring effect (9) has been the subject of considerable discussion (10), (11), (12). Suggested causes have included fluorescence of aerosols and/or trace gases such as NO and NO_2. There is some variation in reported effects, with the possibility of measurement artefacts. Burnett, for example, (8) says that sky light shows Fraunhofer in-filling compared to direct sunlight scattered from paper, while Chanin (12) reports that both sky light and light scattered from the ground show in-filling compared to direct sunlight and sunlight scattered from a "white screen", which are indistinguishable. It may be noted in passing that almost all paper and many paints and textiles contain pontamine and similar fluorescent "whiteners". Chanin also describes effects of season, surface and wavelength, e.g. a weak, spectrally flat effect from oak leaves and a strong, spectrally structured effect for snow. The snow effects are not inconsistent with the scavenging of fluorescent air pollutants by snow. The Ring effect flux of Table 1 follows (8), where Burnett measured the base line shift required to match line shapes for the Na D_2 line in skylight and direct sunlight.

The estimate of 0.1 ppb Rhodamine equivalent is based on (13) and the solar flux figures cited above.

Transmittance Effects

The atmospheric transmittance, at least in the visible, is fairly well known as a function of surface parameters e.g. ref. (14). There are a few weak atmospheric absorption lines close to several of the Fraunhofer lines, but these should be avoidable by judicious selection of filters.

Effects on Pump Radiance

While there is great current interest in the solar flux near the atmospheric U.V. cutoff, an accurate estimate of departures from the synoptic average may be difficult, due to the strong dependence on aerosol and trace gas concentrations.

Conclusions

While there are a variety of atmospheric effects on remote measurement of surface fluorescence, a preliminary survey indicates that they should not amount to more than a few tenths of a ppb Rhodamine equivalent.

R. Dick

TABLE 1
APPROXIMATE VALUES OF UPWARD FLUX AT 590 mm (Na D_2)

VR = 14 km P = .25 Line Center - 5% Continuum

SOURCE	CONTINUUM	LINE CENTRE
Albedo	2.5 E 12	1-2 E 11
N_2 Raman	1.5 E 7	1.5 E 7
Aerosol Fluorescence	1.7 E 6	1.7 E 6
Na Dayglow	0	0-5 E 9
Ring Effect	0-2 E 9	0-2 E 9
0.1 ppb Rh.Eq	1.2 E 10	1.2 E 10

(units are photons/cm^2 sterad sec A)

TABLE 2

DAYGLOW INTERFERENCES

SPECIES	BAND OR LINE	WAVELENGTH (NM)	RELATIVE INTENSITY
Na	D2	588.997	Strong, Variable
H	H-alpha	6563	V weak
OH	(6,1)P	656.8	?
	(6,1)R	656.8	
NO(?)	Continuum	-----	Included in Ring effect
H	H-beta	486.1	Not observed in night glow

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OPTICAL CHARACTERISTICS OF URANYL GEOLOGIC TARGETS,
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Laser-induced fluorescence from the UO_2^{++} ion in a variety of geologic occurrences has been studied as a selective technique for the remote sensing of uranium.[1,2] This study included, in part, the identification of these occurrences and the determination of their optical characteristics.

We have shown that the highly fluorescent UO_2^{++} ion can be found in three types of surface occurrence: bulk uranyl minerals, efflorescent films of uranyl minerals which may be formed along surface exposures of rock through which uraniferous solutions are being transported, and transparent siliceous minerals such as opal, chalcedony, quartz, and calcite.

The excitation and emission spectra, fluorescence lifetimes, and quantum yields were determined for these "targets". These studies have shown that the spectral features of UO_2^{++} ion fluorescence are remarkably similar when excited in bulk mineralization, efflorescent films, and siliceous hosts. Representative spectra are shown in Figure 1. The fluorescence lifetimes of the UO_2^{++} ion in these geologic targets are long compared to most fluorescence from natural occurrences, ranging between 85-600 microseconds. In addition the fluorescence yields can be high, ranging from 0.42-0.8. These data are summarized in Table 1.

Measurements have also been made of the time-dependent fluorescence brightness of over 100 uranyl-bearing and non-uraniferous mineral, rock, and soil samples using pulsed laser excitation at 4250 A and detection within a 50 A handwidth at 5250 A. The relative brightness of the uranyl samples under these conditions was 10^3-10^6 times greater than that of the non-uraniferous samples, with the exception of manganese-bearing zinc silicates from a unique occurrence. Some of these data are shown in Figure 2.[3]

It may be concluded that the high yields, long fluorescence lifetimes, and distinctive spectral features of UO_2^{++} ion fluorescence in geologic targets constitute a "selective window" for their identification with little, if any, interference from other naturally-occurring sources of fluorescence. In addition, the fluorescence brightness of the uranyl-bearing efflorescent films and siliceous targets exhibit a different dependence on the excitation wavelength than does the brightness of bulk uranyl mineralization. This difference may be used to distinguish between such target types.

ROBERT J. L. CHIMENTI

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3. A complete description of the rock, mineral, and soil samples with uranium content and fluorescence data is available from the author upon request.

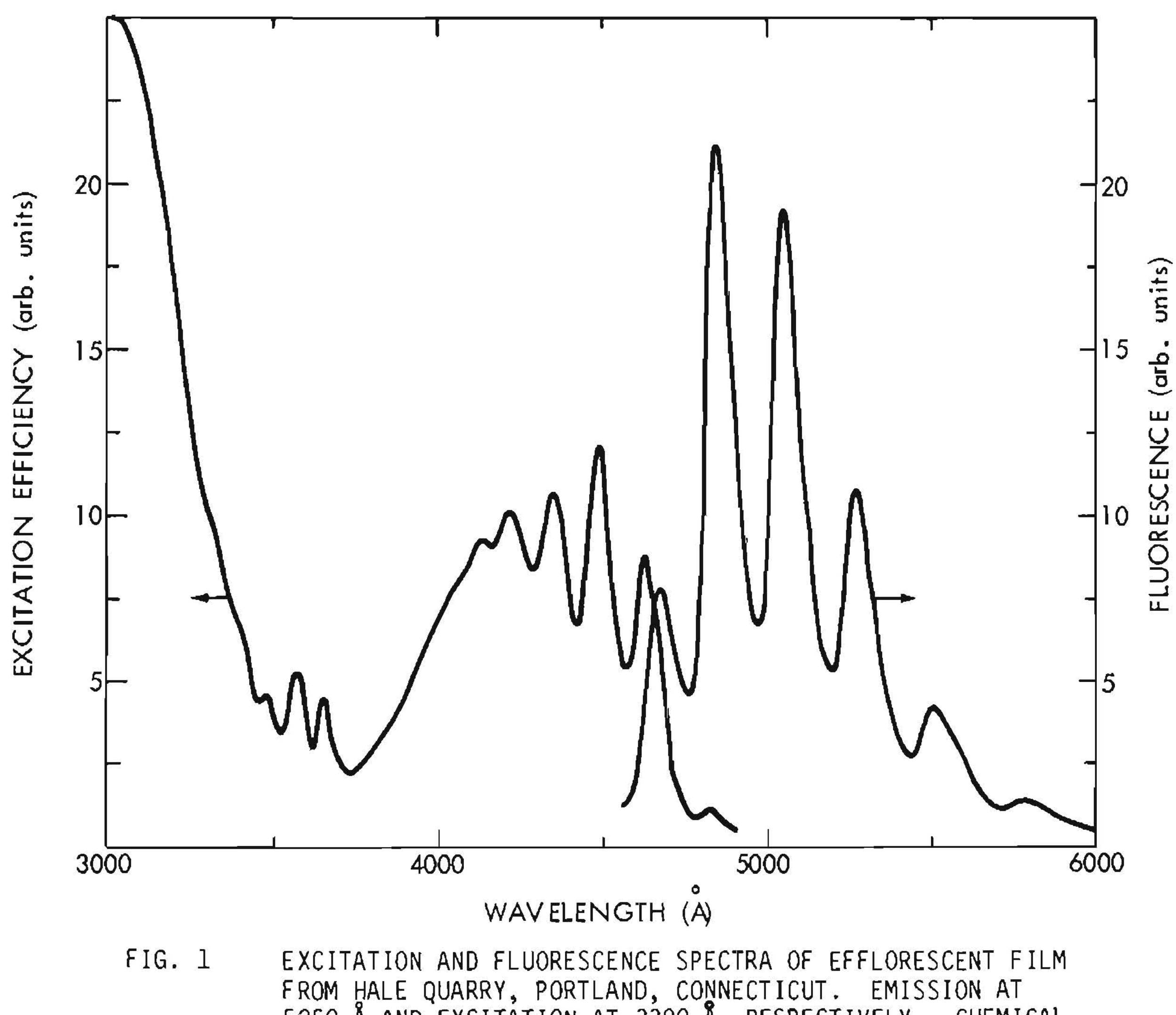

FIG. 1 EXCITATION AND FLUORESCENCE SPECTRA OF EFFLORESCENT FILM FROM HALE QUARRY, PORTLAND, CONNECTICUT. EMISSION AT 5250 Å AND EXCITATION AT 3300 Å, RESPECTIVELY. CHEMICAL URANIUM 420-490 PPM.

TABLE 1

FLUORESCENCE LIFETIMES AND YIELDS FOR URANYL IONS IN ROCKS AND MINERALS

Sample	Lifetime (μs) Range at 298 K	Lifetime (μs) Value at 77 K	Yield
• Uranyl Minerals			
Bulk Minerals			
Andersonite	460-269	800(460)*	0.57
Meta-autunite	85-257	253(188),231(257), 285(228)	0.74,0.8,0.8
Liebigite	400	960	0.42
Schroekingerite	490-571	870(490)	0.56
Meta-uranocircite	171-200	-	-
Efflorescent Films	308-398	-	-
• Uranyl in Siliceous Hosts			
Opals and Silica	171-486	-	-
Glass (1.5 wt.%)	270	570	0.49

*Values in parentheses are the lifetimes measured at room temperature for these samples.

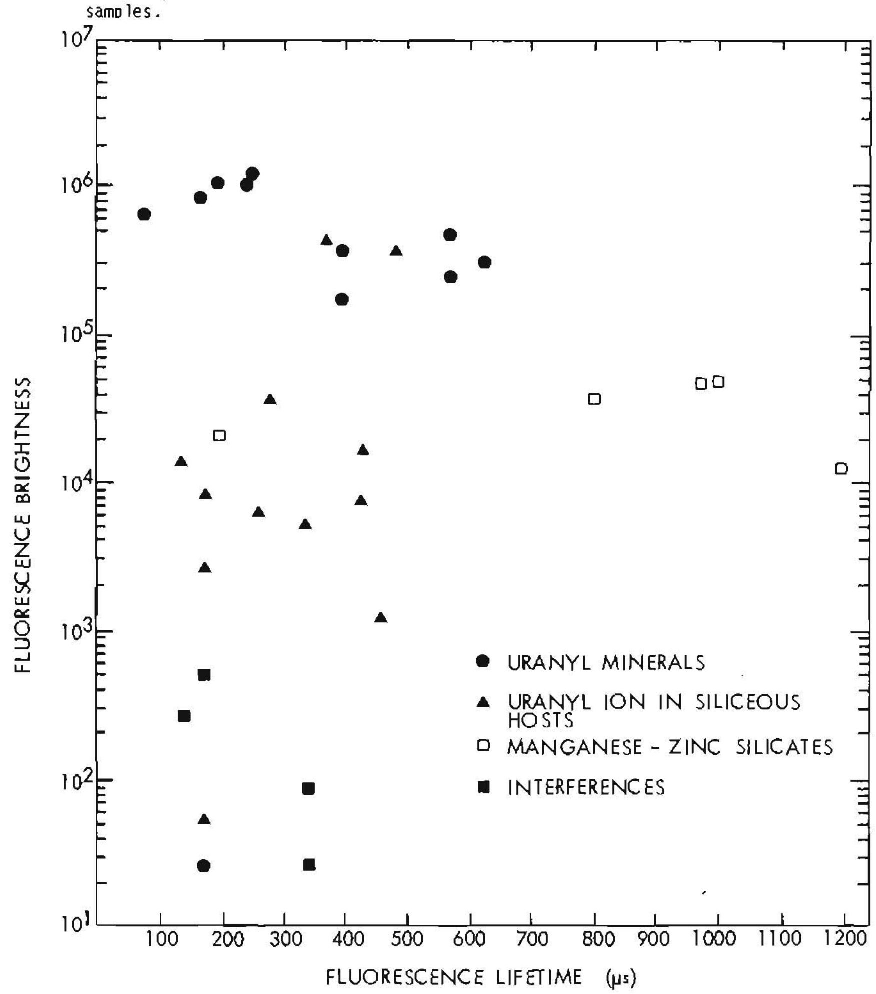

FIG. 2 PEAK FLUORESCENCE BRIGHTNESS FOR PULSED EXCITATION AT 4250 Å AND DETECTION AT 5250 Å WITHIN A 50 Å BANDWIDTH. THE URANYL MINERALS, URANYL IN SILICA, AND Mn-Zn SILICATES EXHIBIT HIGH LEVELS OF BRIGHTNESS IN THIS EXCITATION AND DETECTION "WINDOW". MORE THAN 50 ADDITIONAL SAMPLES GAVE NO DETECTABLE FLUORESCENCE AND ARE NOT SHOWN.[3]

Letter of Invitation

LUNAR AND PLANETARY INSTITUTE
3303 NASA ROAD 1 HOUSTON, TEXAS 77058 CABLE ADDRESS: LUNSI

WORKSHOPS
(713) 486-2173

September 26, 1980

Dear Colleague:

As most of you know, NASA and the Geological Survey have collaborated throughout the 1970's in the design, construction, and field testing of the Fraunhofer line discriminator (FLD), an airborne electro-optical device for the detection of materials stimulated to luminesce by the Sun. Both the prototype instrument and the engineering model FLD, delivered in 1968 and 1974, respectively, were designed to operate from a helicopter as nonimaging luminescence radiometers. Tests were conducted on geochemically stressed trees and drought stressed agricultural crops, oil seeps, rock outcrops, and industrial and residential pollutants. Modifications now permit the engineering model FLD to operate in an imaging mode from fixed-wing aircraft. Analyses of these data show that luminescence is a useful property in discriminating some materials. However, the current imaging system is severely limited because various peripheral components were not designed for imaging and aircraft use, only one Fraunhofer line can be observed at a time, and spatial resolution is awkwardly coarse — 45 m.

We are planning to hold the "Workshop on Applications of Luminescence Techniques to Earth Resource Studies" at the Lunar and Planetary Institute (LPI) in Houston, Texas, December 10-12, 1980. The workshop will address the following questions:

A. What kinds of geological, geobotanical, and crop stress information can be derived from luminescence measurements?

B. To what extent can luminescence measurements complement or supplement information obtained by other sensing techniques?

C. Are there critical gaps in our understanding of luminescence phenomena that currently limit the geological or botanical application of luminescence methods? What types of research need to be conducted in the immediate future to address these questions?

D. To what extent does the current state-of-the-art permit the design of an improved FLD, operating at two or more Fraunhofer lines simultaneously, and having a spatial resolution of 3-5 m from aircraft altitude?

E. 1. Would it be feasible to modify this improved FLD to permit operation from orbital altitude (shuttle sortie 5-7 days) with a spatial resolution of 100 to 200 m?

Luminescence Workshop
September 26, 1980
Page Two

E. 2. How does the atmosphere affect orbital measurement of luminescence on the Earth's surface?

3. Is there experimental evidence to support prediction of success in performing orbital luminescence surveys? Are there predictable physical relationships that would preclude performing luminescence measurements from orbit?

The workshop will consist of a review of the Fraunhofer line discriminator (FLD) technique, the method used to quantify FLD measurements in terms of the luminescent dye standard rhodamine WT, the use of the FLD in measuring the luminescence of various materials, and some conceptual designs of an FLD suitable for use from both aircraft and spacecraft. Ample discussion time will be provided for the questions noted above, as well as related topics, including the use of luminescence for monitoring the areal extent of point source pollutants, and ocean targets. The last session will be devoted to the identification of specific recommendations of the group regarding the continuation of solar stimulated luminescence studies. A tentative agenda is enclosed.

A workshop report volume will be prepared following the meeting and published by the LPI. This volume will contain extended summaries and key figures from all presentaitons prepared by the speakers, plus a synopsis of Session V prepared by the co-chairmen of that session. The synopsis will include a summation of the workshop, specific recommendations made by the group, and a "sense" of the discussion that led to these recommendations.

We are asking all participants to prepare a bibliography of publications they consider to be relevant to the study of solar stimulated luminescence. These bibliographies will be combined to form a list of references to be included in the workshop volume.

You are cordially invited to participate in the workshop. Information on logistics of the workshop and local accomodations is enclosed. Please confirm your intention to attend on the enclosed form and return it to us. We look forward to seeing you in December.

Sincerely,

James Taranik
NASA/Convener

Mark Settle
NASA/Convener

Anthony Barringer
Barringer Research/Program Co-Chairman

William Hemphill
USGS/Program Co-Chairman

Roger Phillips

Roger J. Phillips
Director, LPI
for the Chairmen and Conveners

Enclosures

Program

Session I, December 10, 1980

Remote Sensing of solar stimulated luminescence
Robert D. Watson, Chairman

NASA's interest in the development of remote sensing of luminescence
Mark Settle, NASA Headquarters

Cooperative role of NASA and the Geological Survey in the development of techniques to measure solar stimulated luminescence
William R. Hemphill, U. S. Geological Survey

Functional design of the Perkin-Elmer prototype and engineering model Fraunhofer line discriminators (FLD's)
Fred Gabriel, Perkin-Elmer

Electronic and optical modification of the engineering model FLD, and the evolution of peripheral equipment
Robert D. Watson and A. F. Theisen, U. S. Geological Survey

Session II, December 10, 1980

Experimental use of the FLD in the detection of natural and manmade materials
William R. Hemphill, Chairman

Quantification of luminescence intensity in terms of a rhodamine WT standard
Robert D. Watson, U. S. Geological Survey

Experimental use of luminescence to identify moisture stressed vegetation and potential significance to geochemically induced plant stress
Ray Jackson, Dept. of Agriculture

Airborne delineation and luminescence measurement of point source pollutants
Craig McFarlane, Environmental Protection Agency

Airborne FLD surveys in Nevada, southern California, and central New Mexico
Robert D. Watson, U. S. Geological Survey

Application of Fraunhofer luminescence to offshore petroleum exploration and marine pollution
Mitchell Henry, U. S. Geological Survey

Aerial survey of luminescent rocks, Lisbon Valley, Utah
Preston Niesen, Atlas Minerals

Airborne use of the FLD to delineate luminescent rock materials in the California desert
Jean Juilland, Bureau of Land Management

Measurement of shock induced luminescence at Meteor Crater with laboratory and airborne systems
David J. Roddy, U. S. Geological Survey

Digital image processing of FLD data
Pat Chavez, U. S. Geological Survey

Session III, December 11, 1980

Conceptual design of an FLD suitable for use from both aircraft and satellite, with consideration of laser systems
John DeNoyer,Chairman

The MK II Fraunhofer line discriminator for airborne and orbital remote sensing of solar-stimulated luminescence
Sherman K. Poultney, Perkin-Elmer

Optical design considerations of an orbital FLD
Philip N. Slater, University of Arizona

Proposed design for an aircraft and Space Shuttle compatible FLD
Robert D. Watson, U. S. Geological Survey

A correlation spectrometer approach for an FLD design
Robert Dick, Barringer Research

Atmospheric considerations in measuring the luminescence of Earth materials from space
Robert Dick, Barringer Research

Session IV, December 11, 1980

Open discussion of alternate techniques, and possible future research activities for luminescence applications
Mark Settle, Chairman

Discussion topics:

A. *Other remote sensing techniques in the visible and near visible spectrum which may complement FLD measurements*
Alex Goetz, JPL, Discussion Leader

B. *Feasibility and desirability of experimental registry of FLD imagery with data from other remote sensors*
John DeNoyer, USGS, Discussion Leader

C. *Fluorescence of the uranyl ion in geologic targets*
Robert J. L. Chimenti, Exxon Research, Discussion Leader

D. *Test site experiments: agriculture, point source pollutants, and estuarine sites*
Ray Jackson, Dept. of Ag.; Craig McFarlane, EPA; Discussion Leaders

E. *Other*

Session V, December 12, 1980

Workshop summation; open discussion and identification of specific comments and recommendations regarding the continuation of solar stimulated luminescence studies
Anthony Barringer and Thomas McCord, Co-Chairmen

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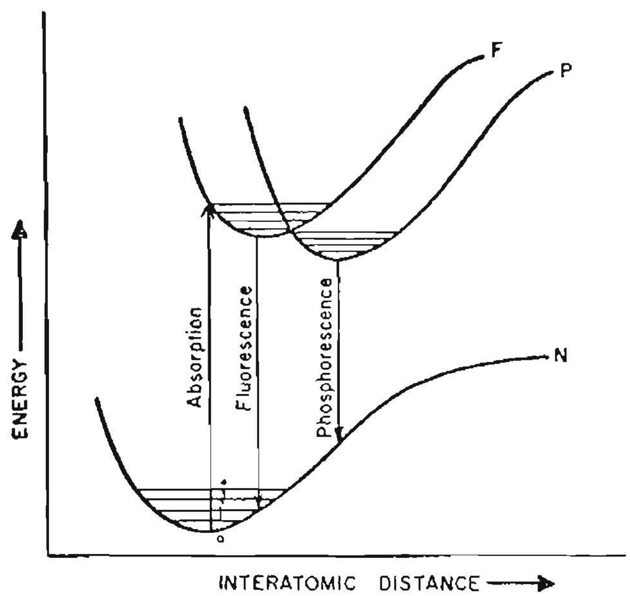
Definitions

Luminescence - Emission of light in the visible and near visible part of the spectrum caused by absorption of electromagnetic energy (visible light, ultraviolet, x-rays, gamma rays), energy of charged particles (electrons, protons), or electrical, mechanical, and chemical reactions. Emitted light normally is of lower energy than the energy absorbed. Luminescence is a general term which includes fluorescence and phosphorescence.

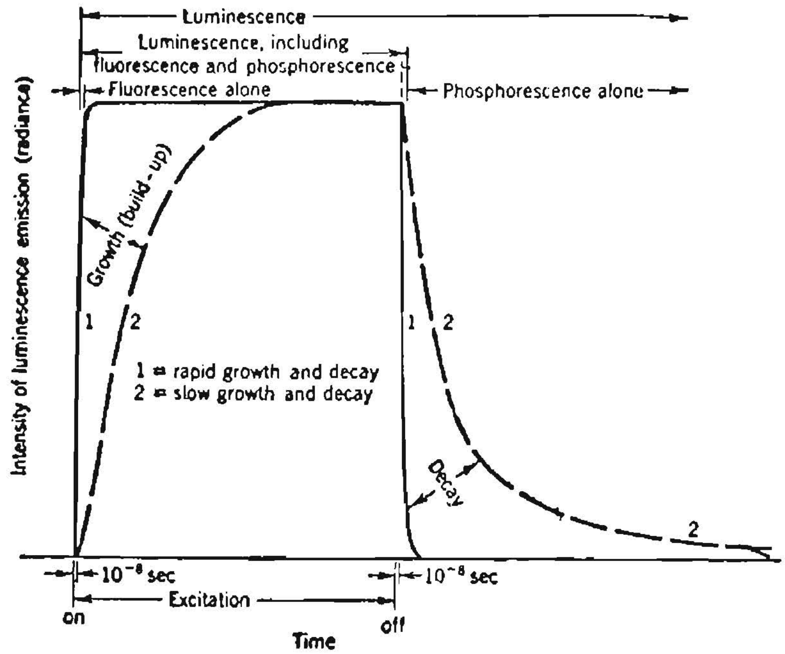
Fluorescence - Emission of light from substances only during the time they are exposed to radiation. See absorption and fluorescence in energy level diagram below. A molecule in the excited state F (called the "singlet" state by spectroscopists) has a lifetime on the order of 10^{-8} seconds.

Phosphorescence - Persistence of emission after the exciting radiation is cut off. This involves electron transitions from the excited state, F (see energy level diagram below), to a somewhat lower energy excited state, P (called the "triplet" state by spectroscopists). Molecules in the excited state, P, can return to the ground state, N (therein emitting light), but the probability of this occurring is less than the F-N transition for fluorescence. The excited state will exceed 10^{-8} seconds, and phosphorescence may persist several seconds, minutes, or longer. An electron transition from P to N via F is also possible, but the probability of this occurring is even less than the P-N transition.

Energy level diagram of molecule -- Shows ground state, N, excited states F and P, and vibrational levels (0, 1, 2, 3, and 4) of each state.



Time relationships of luminescence (modified from Leverenz, 1950, p. 150)-



Quantum yield of luminescence -- Number of photons emitted to those absorbed.

Excitation spectrum - Plot of the intensity of luminescence at a fixed wavelength as a function of the wavelength of exciting light. With a fluorescence spectrometer, the emission monochromator would be fixed at, say, a particular Fraunhofer line, and the excitation monochromator would be scanned.

Emission spectrum - Plot of the intensity of excitation as a function of the wavelength of the emitted light. With a fluorescence spectrometer, the excitation monochromator would be fixed, and the emission monochromator would be scanned.

Fraunhofer lines - Dark lines in the solar spectrum caused by selective absorption of light by gases in the relatively cool upper part of the solar atmosphere.

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